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THEORY OF DEMLO NUMBERS

By

K. R. GUNJIKAR AND D. R. KAPREKAR

1. In the last Physical Sciences number of the University Journal (Vol. VII, Part 3, Nov. 1938), a paper on Demlo numbers, giving their definition and some of their interesting properties, was published by one of us (D. R. Kaprekar). That paper will be referred to as D. N. I. In this paper a brief theoretical discussion of the same is undertaken.

2. NOTATION

(1) A number formed by the digits $a, b, c, \dots, k$, from left to right will be denoted by $a, b, c, \dots, k$, with intervening commas to distinguish it from their product $a.b.c.\dots.k$. (The commas are not necessary when the actual arithmetical digits are given).

(2) The number $m, m, m, \dots$ repeated n times will be denoted by m_n . m_n may form part of a bigger number, in which case, it will be separated from the rest by commas. Thus we may write 5_4 for 5555 ; or $23, 4_3, 67$ for 2344467.

3. DEFINITIONS

A Demlo number D consists of three parts, a left part L , a middle part M , and a right part R , satisfying the following conditions :—

- (a) The middle part M is of the form m_n , ($1 \leq m \leq 9$).
- (b) L and R have the same number of digits p . (If L has one digit less than R , a zero can be added to it on the left to satisfy this condition).
- (c) $L+R=m_p$, m being the same digit as in (a), and p the number of digits in R .

Thus $D = L, m_n, R$, where $L+R=m_p$, e.g. $23, 7_4, 54$ is a Demlo number, with $L=23$, $M=7_4=7777$, $R=54$, since $L+R=77=7_2$. Similarly $94, 6_3, 572$ is a Demlo number, with $L=094$.

NOTE.—(1) The middle part may be absent altogether, as in $23, 54$. Here $m=7$ but $n=0$.

(2) L and R may both be absent, in which case the number is called a linear Demlo number, e.g. 7_4 is a linear Demlo number. This may also be regarded as $0, 7_4, 7$.

(3) If $L+R=m_{p+1}$, where p =number of digits in R , L, m_n, R is *not* a Demlo number. Thus 166,111,945 is not a Demlo number.

(4) It is unnecessary to consider forms for L , with 2 or more digits less than in R . For in such a case it is obvious that one or more left-hand digits of R will be identical with m and so can be added to m_n .

4. GENERAL EXPRESSION

A linear Demlo number $m_n=m, m, m, \dots$ n times.

$$\therefore m_n = m \times 1_n \quad (4.1)$$

$$= m \times (10^{n-1} + 10^{n-2} + \dots + 10 + 1) \\ = m \times (10^n - 1)/9 \quad (4.2)$$

In particular,

$$9_n = 10^n - 1 \quad (4.21)$$

Since a general Demlo number $D=L, m_n, R$, where $L+R=m_p$, p being the number of digits in R ,

$$D = R + m_n \times 10^p + L \times 10^{n+p} \\ = (m_p - L) + m_n \times 10^p + L \times 10^{n+p} \\ = m \times (10^p - 1)/9 + m \times (10^n - 1) \times 10^p/9 + L(10^{n+p} - 1) \\ \text{by 4.2}$$

$$= \left(L + \frac{m}{9} \right) (10^{n+p} - 1) \quad (4.3)$$

$$= (9L + m) \times 1_{n+p} \quad (4.4)$$

5. PROPERTIES OF DEMLO NUMBERS

Every Demlo number has a factor of the type 1_k , where $k=n+p$ =the number of digits in M, R . (5.1).

This follows immediately from 4.4.

The converse of (5.1) is true with certain limitations and may be stated as follows :—

$A \times 1_k$, where A is any number, is a Demlo number for sufficiently large values of k . (5.2).

Proof: If $A \times 1_k$ is a Demlo number L, m_n, R ,

$$A = 9L + m \quad \text{by (4.1)} \quad (5.3)$$

$$\text{Then } m \equiv A \pmod{9}, 1 \leq m \leq 9 \quad (5.4)$$

$$\text{and } L = \frac{A - m}{9} \quad (5.5)$$

To find R , let the number of digits in L be q .

$$\text{Then if } L < m_q, R = m_q - L; \text{ otherwise } R = m_{q+1} - L. \quad (5.6)$$

If the number of digits in $m_k - L$ be less than q , R must be taken with the necessary number of zeros added on the left to equalize them.

Finally the number of digits in m_n is given by $n = k - p$ (5.7)

This shows that $k \geq p$; otherwise n being negative $A \times 1_k$ is not a Demlo number.

Examples.

(1) $4931 \times 1_k$.

Here $A = 4931 = 9 \times 547 + 8$.

$\therefore L = 547, m = 8, R = 888 - 547 = 341$ and $p = 3$.

$\therefore 4931 \times 1_k$ is a Demlo number for $k \geq 3$.

$k = 2$ gives 5424 which is not a Demlo number.

For $k \geq 3, 4931 \times 1_k = 547, 8k-8, 341, \text{ a D. N.}$

(2) $662 \times 1_k$.

Here $L = 073, m = 5, R = 555 - 073 = 482$ and $p = 3$.

$\therefore 662 \times 1_k = 73, 5k-5, 482$ if $k \geq 3$.

(3) $7721 \times 1_k = 857, 8k-8, 031$ for $k \geq 3$.

(4) $5175 \times 1_k = 574, 9k-9, 425$ for $k \geq 3$.

6. WAYS OF OBTAINING DEMLO NUMBERS

In D. N. I, a number of ways of obtaining Demlo numbers were given. It will be seen that they all reduce to the application of 5.2 in different ways, though the reservation re. the value of k is not stated there in all cases. We shall consider here only one or two cases for illustration.

(1) Processes of conical tables.

Table No. 1.

1 $\times 9 + 2 = 1$
12 $\times 9 + 3 = 111$
123 $\times 9 + 4 = 1111$

...

123,..., $k \times 9 + (k+1) = 1_{k+1}$
 $1 \leq k \leq 9$

Table No. 2.

0 $\times 9 + 8 = 8$
9 $\times 9 + 7 = 88$
98 $\times 9 + 6 = 888$

...

987,..., $l \times 9 + (l-2) = 8_{l-1}$
 $1 \leq l \leq 9$

For

1234,..., $k = 1_k + 1_{k-1} + 1_{k-2} + \dots + 1$
 $= (9_k + 9_{k-1} + \dots + 9)/9$

$\therefore 123, \dots, k \times 9 = 10^k + 10^{k-1} + \dots + 10^1 - k$ by (4.2)
 $= 1_{k+1} - k - 1$

$\therefore 1234, \dots, k \times 9 + (k+1) = 1_{k+1}$ (6.1)

$$\begin{aligned}\text{Similarly } 987, \dots, l &= 9_{10-l} - 123, \dots, (9-l) \\ &= 9_j - 123, \dots, (j-1)\end{aligned}$$

Where $j = 10 - l =$ number of digits in $987, \dots, l$.

$$\begin{aligned}\therefore 987, \dots, l \times 9 &= 9 \times 9_j - 123, \dots, (j-1) \times 9 \\ &= 9 \times (10^j - 1) - 1_j + j \quad \text{from (6.1)} \\ &= 9, 0j - 1_j + j - 9 \\ &= 8_j, 9 - 1 + j - 8\end{aligned}$$

$$\therefore 987, \dots, l \times 9 + (l-2) = 8_{j+1} + j - 8 + l - 2 = 8_{11-l} \quad (6.2)$$

(2) The recurring decimal part of $1/N$, where N is prime to 2 and 5, multiplied by N , is a linear Demlo number 9_n , n being the number of recurring digits.

Let $\frac{1}{N} = 0.\dot{a}, \dot{b}, \dot{c}, \dots, \dot{i}$, since there is no non-recurring part when N is prime to 2 and 5.

Then $\frac{10^n}{N} = a, b, c, \dots, l. \dot{a}, \dot{b}, \dot{c}, \dots, \dot{i}$, where $n =$ number of the recurring digits $a, b, \dots, k$.

$$\therefore (10^n - 1) = N \times a, b, c, \dots, l.$$

$$\text{i.e. } N \times a, b, \dots, l = 9_n. \quad (6.3)$$

This is also obvious if we note that $1 = 0.\dot{9}$.

Again if N is a prime different from 2 or 5 and the number of recurring digits is even, say $2k$, then the recurring part itself is a Demlo number.

For

$$a, b, \dots, l \times N = 9_{2k} = 10^{2k} - 1 \quad \text{by (6.3)}$$

$$\therefore a, b, \dots, l = (10^k + 1)(10^k - 1) / N$$

Now N cannot be a factor of $10^k - 1$, otherwise the number of recurring digits would be k and not $2k$.

$$\therefore N \text{ is a factor of } 10^k + 1$$

$$\text{i.e. } \frac{10^k + 1}{N} = \text{an integer, } A \text{ say.}$$

$$\therefore a, b, \dots, l = A \times (10^k - 1) = 9A \times 1_k, \text{ a Demlo number provided } k \geq p, \text{ the number of digits in } R \quad \text{by (5.7)}$$

This condition is satisfied, since $p \leq k$.

Corollary: If the number of digits n in the recurring part can be factorized i.e. if $n = p \times q \times \dots \times r$ say, then $a, b, \dots, l$ is divisible by $9_p; 9_q; \dots, 9_r$.

e.g., 032258064516129 the recurring part of $\frac{1}{31}$ contains 15 digits and so is divisible by 999 and 99999,

7. WONDERFUL DEMLO NUMBERS

A number of the type

$$123, \dots, k, (k-1), (k-2), \dots, 321, 1 < k \leq 9,$$

where the digits ascend and descend by differences of 1, is called a Wonderful Demlo number.

A wonderful Demlo number $W=123, \dots, k, \dots 321$ is a perfect square $=(1k)^2$.

Here $L=123, \dots, k-1$, $m=k$, $p=k-1$, $n=1$.

$$\begin{aligned} \therefore W &= (9L+m) \times 1_{n+p} && \text{by (4.4)} \\ &= \{9 \times 123, \dots, (k-1) + k\} \times 1_k && \text{since } n+p=k \\ &= 1_k \times 1_k && \text{by (6.1)} \end{aligned}$$

$$\therefore W = (1k)^2 \quad (7.1)$$

A most striking property of these numbers was stated in D. N. I and is proved in a paper by one of the authors (D. R. K.) in the Mathematics Student, Vol. 6, June 1938. It is proved here again by a different method.

Partition and insertion property

Dissectible numbers. This is a set of numbers, of the form a, b, c , such that when any one of them is multiplied by a Wonderful Demlo number, the product takes the form a, x, b, y, c . (a or b or both may be zero)

$$\text{e.g. } 162 \times 121 = 1, 9, 6, 0, 2; \quad 162 \times 12321 = 1, 99, 6, 00, 2.$$

We shall now investigate the conditions to be satisfied by dissectible numbers.

For simplicity let us consider $1234321 \times a, b, c$, a, b, c being a dissectible number.

By the usual form of the operation of multiplication

$$\begin{array}{r} 1234321 \\ \times a, b, c \end{array}$$

$$\begin{array}{r} c, (2c), (3c), (4c), (3c), (2c), c \\ b, (2b), (3b), (4b), (3b), (2b), b \\ a, (2a), (3a), (4a), (3a), (2a), a \end{array}$$

$$\begin{array}{r} a, (2a+b), (3a+2b+c), (4a+3b+2c), (3a+4b+3c), (2a+3b+4c), \\ (a+2b+3c), (b+2c), c. \end{array}$$

Here the terms in the brackets may have more than one digit, but they have their place value.

If a, b, c is a dissectible number,

(i) $2a+b \not\geq 9$ for otherwise the left-hand-most digit of the product will differ from a . It will be seen later that $2a+b \leq 8$.

(ii) $b+2c > 9$.

For if $b+2c \leq 9$, since 3rd digit from the right must be $b+2c$, $a+2b+3c = b+2c+10$

i.e. $a+b+c=10$, requiring 1 to be carried over.

Then 4th digit from right $= 2a+3b+4c+1-20$
 $= b+2c+1 \neq b+2c$

$\therefore b+2c > 9$. (7.2)

Let $b+2c = 10+y$, $0 \leq y \leq 9$

Then the 2nd digit from the right $= y$

„ „ 3rd
 $= a+2b+3c+1$ - greatest multiple of ten
 $= y+10+a+b+c+1$ - g. m. t.
 $= y$ if $a+b+c=9$ or 19
 carrying over 2 if $a+b+c=9$
 and 3 if $a+b+c=19$

If $a+b+c=19$

Then 4th digit $= 2a+3b+4c+3$ - g. m. t.
 $= b+2c+38+3$ - g. m. t.
 $= y+1+40$ - g. m. t.
 $\neq y$.

$\therefore a+b+c=9$ (7.3)

Then 4th digit $= 2a+3b+4c+2$ - greatest multiple of ten.
 $= b+2c+20$ - g. m. t.
 $= y+30$ - g. m. t.
 $= y$ carrying over 3.

Then 5th digit $= 3a+4b+3c+3$ - g. m. t.
 $= b+30$ - g. m. t.
 $= b$ carrying over 3.

Then 6th digit $= 4a+3b+2c+3$ - g. m. t.
 $= 2a+b+1+20$ - g. m. t.
 $= 2a+b+1$ carrying over 2 if $2a+b \leq 8$.

Then 7th digit $= 3a+2b+c+2$ - g. m. t.
 $= 2a+b+1+10$ - g. m. t.
 $= 2a+b+1$ carrying over 1.

Then 8th digit $= 2a+b+1$

and 9th digit $= a$

$\therefore$ Product $= a, (2a+b+1)_s, b, (b+2c-10)_s, c$

If $2a+b=9$, then 6th digit=0 carrying over 3.

and 7th digit $=3a+2b+c+3-\text{g. m. t.}$
 $=21-\text{g. m. t.}$
 $=1 \neq 6\text{th digit.}$

$$\therefore 2a+b \leq 8. \quad (7.4)$$

It can be seen that the same conditions must be satisfied for the product by any wonderful Demlo number.

Thus a dissectible number a, b, c satisfies the following conditions:—

- (i) $a+b+c=9$;
- (ii) $b+2c>9$ i.e. $a<c$ from (i) ;
- (iii) $2a+b \leq 8$ or $c \geq a+1$ and $a \leq 4$.

We thus obtain the following 25 dissectible numbers only.

009; 018; 027; 036; 045; 054; 063; 072; 081;
 108; 117; 126; 135; 144; 153; 162;
 207; 216; 225; 234; 243;
 306; 315; 324;
 405;

When a, b, c is multiplied by any wonderful Demlo numbers, the product,

$$123, \dots, l, \quad k-1, \dots, 321 \times a, b, c \\
= a, (2a+b+1)_{k-1}, b, (b+2c-10)_{k-1}, c.$$

This discussion is sufficient to show the great variety of interesting properties possessed by Demlo numbers. Other properties will be considered theoretically later on.

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PRODUCTS OF SOME LINEAR 'DEMLO' NUMBERS

By

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(Communicated by Professor M. L. Chandratreya)

*I. The object of the article:—*The object of this article is to discuss the product of one number consisting of one and the same digit repeated a certain number of times and another number consisting of some other digit repeated in it the same number of times, e.g. 5555×7777 or 44444×88888 .

Such numbers will be represented by $(r)_n$ and $(r')_n$. r and r' are the different digits and they are each repeated n times in the two numbers respectively. $(r)_n$ means r is repeated n times and $(r')_n$ means r' is repeated n times.

r and r' can have any value from 1 to 9. If r and r' are the same, the product $(r)_n \times (r')_n = (r)_n^2$. Now $(r)_n \times (r')_n$

$$= r \times (1)_n \times r' \times (1)_n$$

$$= rr' \times (1)_n^2.$$

Here rr' is the product of r and r' . The whole problem thus reduces to finding the multiplication of rr' with $(1)_n^2$. We shall first state briefly a method for writing down the value of $(1)_n^2$ without going into any theoretical discussion. The method is divided in two stages (i) for $n \leq 9$ and (ii) $n \geq 10$.

*II. The value of $(1)_n^2$ when $n \leq 9$:—*The following nine squares can be easily verified and remembered. In each the digits go on increasing from one and come down to one, the highest digit reached being the value of n from one to nine respectively.

$$(1)_1^2 = 1$$

$$(1)_2^2 = 121$$

$$(1)_3^2 = 12321$$

$$(1)_4^2 = 1234321$$

$$(1)_8^2 = 123456787654321$$

$$(1)_9^2 = 12345678987654321$$

These and other such numbers have been designated by me somewhere else as Wonder Demlo Numbers.

*III. Some Terminology :—*When $n \leq 9$ the above nine values are the values of $(1)_n^\alpha$ and they will be referred to as the values of $(1)_\alpha^\alpha$ where α has some value from one to nine.

If the value of $(1)_\alpha^\alpha$ is written down and the unit digit is omitted, the part left will be called by the letter L. Thus if $\alpha=3$, $(1)_3^3=12321$ and then $L=1232$. If $\alpha=5$, $(1)_5^5=123454321$ and then $L=1234532$ etc. If $\alpha=1$ then L does not exist for $(1)_1^1=1$.

The unit digit omitted will be called R. We have in all the cases given above $R=1$.

The next term to be explained is lgr. lgr is a short form of *left gap repeater*. There is a certain group of digits which will be repeated again and again and it will find its place on the left side of the product to be found. Also there will be a certain other group of digits repeated again and again on the right side of the product to be found. It will be called as *right gap repeater* and denoted shortly as Rgr.

When n is greater than 9 express it as $9k+\alpha$ where α is not to be zero and can have any value from 1 to 9. Thus if $n=15=9 \times 1+6$, $k=1$ and $\alpha=6$. Again if $n=28=9 \times 3+1$, $k=3$ and $\alpha=1$. Take $n=18=9 \times 2+0$. This is not allowed and we must write it as $9 \times 1+9$ and here $K=1$ and $\alpha=9$. When $n=27$ it is not taken as $9 \times 3+0$ but as $9 \times 2+9$ and the value for K is 2 and that of α is 9.

*IV. The value of the product $(1)_n^\alpha$ when $n \geq 10$:—*Without going into a formal theoretical proof the result only may be stated here. It is as follows :

$$(1)_n^\alpha = (\text{lgr})_k \text{ L } (\text{Rgr})_k \text{ R.}$$

Where $(\text{lgr})_k$ means the repeated value of the group (lgr), k times ; with a similar meaning for $(\text{Rgr})_k$. Also all the digits in the formula are to be put side by side in that order and in their respective places. Thus $(32)_2 85 (17)_1 1$, means the number 32328517171. -

In all these values to be found always take $(\text{lgr})=123456790$ (mark the absence of 8) and $(\text{Rgr})=098765432$ (mark the absence of 1). The value of L is to be found from α and the value of R is already given as 1.

Find the value of α and K and also the value of L from the given value of n and taking for granted the value of lgr and Rgr repeat them K times in their proper places with respect to the positions of L and R and we have the value of $(1)_n^2$.

Thus to find $(1)_{14}^2$. $14=9 \times 1 + 5$. Here $K=1$ $\alpha=5$ and because $\alpha=5$, $L=12345432$, $R=1$ $lgr=123456790$, $Rgr=098765432$ and hence we get

$$(1)_{14}^2 = \underbrace{123456790}_{lgr} \underbrace{12345432}_L \underbrace{098765432}_R \underbrace{1}_R$$

To find $(1)_{21}^2$, $n=21=9 \times 2 + 3$, giving $K=2$, $\alpha=3$ and hence $L=1232$ and $R=1$. As $K=2$ we have to repeat the value of (lgr) and (Rgr) twice. Thus

$$(1)_{21}^2 = (123456790)_2 1232 (098765432)_2 1.$$

One more example to show that α cannot be made zero is given. Thus to find $(1)_{18}^2$. Here $18=9 \times 1 + 9$ (not $9 \times 2 + 0$) giving $K=1$ $\alpha=9$ and $L=1234567898765432$, $R=1$.

$$\text{Hence } (1)_{18}^2 = \underline{123456790 \ 1234567898765432 \ 098765432 \ 1}$$

V. Basis of the method to find $(r)_n \times (r')_n$:— It is already seen that $(r)_n \times (r')_n = rr' \times (1)_n^2$. We know now the value of $(1)_n^2$. We have only to multiply the result by rr' . It took me some years before I could suitably discover the solution of the problem. The problem is divided for convenience into four separate parts :—

- (i) When rr' is a multiple of 9.
- (ii) When rr' is a multiple of 3 or 6 but not of 9 or 10.
- (iii) When rr' is not a multiple of 3, 6, 9 or 10.
- (iv) When rr' is a multiple of 10.

VI. Some Remarks :—

(A) The same product rr' can be formed at the same time in some cases in more than one way. Thus $18=9 \times 2$ or 6×3 . $24=8 \times 3$ or 6×4 . As r and r' are digits we are not taking account of the product $24=12 \times 2$ or 24×1 , thus keeping the values of r and r' as having only single digits. In spite of this, it will be seen that

the value of $(r)_n \times (r')_n$ can sometimes be the value of two different multiplications. Thus

$$4444 \times 6666 \text{ and } 8888 \times 3333.$$

are only two multiplications in appearance and their values are the same each equal to $24 \times (1)_4^2$.

(B) The product $(r)_n \times (r')_n$ can always be expressed in the following form:—

$$(r)_n \times (r')_n = (\text{lgr})_k \text{ L } (\text{Rgr})_k \text{ R}.$$

The constants L and R are fixed constants. R is a number only of one digit, L is a number having digits 0 to 18 in that number. The digits depend on the value of α which in some way is similar to that described in finding the value of $(1)_n^2$. (lgr) and (Rgr) are repeating groups and they will repeat K times as pointed out before.

(C) The number of digits in (lgr) and (Rgr) are found to obey some fixed laws:—

- (i) When rr' is a multiple of 6 or 3 but not of 9 or 10 they each contain 3 digits.
- (ii) When rr' is not a multiple of 3, 6 or 9 or 10 the number of digits in each are always 9.
- (iii) When rr' is a multiple of 9 (lgr) and (Rgr) both consist of only one digit each.
- (iv) When rr' is a multiple of 10, the problem reduces to one of the above with a 0 at the right side.

VII. The product $(r)_n \times (r')_n$ when rr' is a multiple of nine:—Express $rr' = 9t$ and take $(\text{lgr}) = t$ $(\text{Rgr}) = 9 - t$

$$K = n - 1$$

$$L = t - 1$$

$$R = 10 - t.$$

Thus the general formula

$$(r)_n \times (r')_n = (\text{lgr})_k \text{ L } (\text{Rgr})_k \text{ R}$$

gives $(r)_n \times (r')_n = (t)_{n-1} (t-1) (9-t)_{n-1} (10-t).$

In *e.g.* $(6)_8 \times (3)_8$ *i.e.* 66666×33333 $rr' = 18 = 9 \times 2$ and therefore $t = 2$, $n = 5$ and therefore $K = 4$, $L = 1$ and $R = 8$ and the value of the product is $(2)_4 1 (7)_4 8 = 222217778$.

The other factors of 18 are 9 and 2 and so the above result is also the value of $(9)_8 \times (2)_8 = (99999) \times (22222)$.

Let us find $(6)_7^2$. Here $rr' = 36 = 9 \times 4$. Hence $t = 4$, $K = 6$, $L = 3$, $R = 6$ $(lgr) = 4$ $(Rgr) = 5$ and the product becomes

$$(4)_6 3 (5)_6 6 = 44444435555556.$$

In $(8)_4 \times (9)_4$, $t = 8$ $L = 7$, $K = 3$ $R = 2$, $(lgr) = 8$, $(Rgr) = 1$

Hence $(8)_4 \times (9)_4 = 88871112$.

The following results are good corollaries:—

$$(9)_n^2 = (9)_{n-1} 8 (0)_{n-1} 1$$

$$(6)_n^2 = (4)_{n-1} 3 (5)_{n-1} 6$$

$$(3)_n^2 = (1)_{n-1} 0 (8)_{n-1} 9$$

$$(3)_n \times (6)_n = (2)_{n-1} 1 (7)_{n-1} 8.$$

(A theoretical discussion of this section with some aspects can be seen in the writer's article on 'Wonderful Demlo Numbers' I. M. S's Magazine Student Vol. VI, pp. 68-70).

*VIII. The product $(r)_n \times (r')_n$ when rr' is a multiple of 3 or 6 but not of 9 or 10:—*When $n \leq 3$ it can take any value $\alpha = 1, 2, 3$. In table No. I values of these products are given under arguments α and rr' . Thus when $\alpha = 2$ and $rr' = 21$ we get 2541. This is the product of $(7)_3 \times (3)_3$. If we want to find the product $(8)_3 \times (3)_3$ *i.e.* 888×333 , then $\alpha = 3$ and $rr' = 24$. The table gives 295704. This is the required product.

When $n \geq 4$ express n as $3K + \alpha$ (the value of zero for α being excluded) and then K gives the number of repetitions of (lgr) and (Rgr) . α determines the number from the tables which when deprived of its unit digit is the quantity L and the unit digit itself the value of R . The values of (lgr) and (Rgr) are to be taken from the same table. Having thus determined the values of $K, L, R, (lgr), (Rgr)$, the product is given by the formula already quoted, *viz.* :—

$$(r)_n \times (r')_n = (lgr)^K L (Rgr)^K R.$$

TABLE NO. I

rr'	$\alpha=1$	$\alpha=2$	$\alpha=3$	(lgr)	(Rgr)
3 (1×3)	3	363	36963	370	296
6 (1×6) (2×3)	6	726	73926	740	592
12 (2×6) (4×3)	12	1452	147852	148	185
15 (5×3)	15	1815	184815	185	481
21 (3×7)	21	2541	258741	259	074
24 (3×8) (6×4)	24	2904	295704	296	370
42 (7×6)	42	5082	517482	518	148
48 (8×6)	48	5808	591408	592	740

Thus to find the value of 7777×6666 i.e. $(7)_4 \times (6)_4$. Here $n=4=3 \times 1 + 1$ giving $k=1$ and $\alpha=1$. $rr'=42$. Arguments $\alpha=1$ and $rr'=42$ gives $L=4$ and $R=2$. (lgr) and (Rgr) for 42 are 518 and 148 respectively. Hence

$$(7)_4 \times (6)_4 = 51841482$$

Let us find $(7)_{11} \times (6)_{11}$. Here $n=11=3 \times 3 + 2$ giving $k=3$ and $\alpha=2$. Arguments $\alpha=2$ $rr'=42$ give 5082. Hence $L=508$. $R=2$ and the values of (lgr) and (Rgr) are 518, 148 respectively as before. Hence the product is

$$5185185185081481481482$$

Another example may be given. In $(3)_{12} \times (2)_{12}$ $n=12=3 \times 3 + 3$ and not $3 \times 4 + 0$. This gives $k=3$, and $\alpha=3$. Arguments $\alpha=3$ and $rr'=6$ give 73926. Hence $L=7392$ and $R=6$, (lgr) and (Rgr) from the table are 740 and 592. Hence the product is

$$(740)_3 7392 (592)_3 6.$$

consider another peculiar case of $(3)_7 \times (2)_7$. Here $n=7=3 \times 2 + 1$ giving $k=2$ and $\alpha=1$ Arguments $\alpha=1$ and $rr'=6$ give the number 6. Thus L does not exist and $R=6$ (L should not be considered as zero). The product thus is given by 7407405925926.

IX. Product $(r)_n \times (r')_n$ when rr' is not a multiple of 3, 6, 9 or 10:—Here again the method is similar and divided into two parts (i) for $n \leq 9$ and (ii) for $n \geq 10$. Table No. II gives values for arguments $\alpha=1, 2 \dots 9$ and rr' . There are only 15 values of rr' that can occur and these are 1, 2, 4, 5, 7, 8, 14, 16, 28, 32, 25, 35, 49, 56 and 64. The case of $rr'=1$ is the same as $(1)_n^2$ and it is already discussed.

When $n \geq 10$, we express it as $9k + \alpha$ and the arguments α and rr' will enable us to decide the value of $rr' \times (1)_\alpha^2$. This value deprived of its unit digit is taken as L and the unit digit is taken as R. The corresponding values of (lgr) and (Rgr) are given in Table No. III for the argument rr' . When thus α , K, L, R, (lgr) and (Rgr) are determined, the value of the product is written out as before by the general formula

$$(r)_n \times (r')_n = (\text{lgr})_k L (\text{Rgr})_k R.$$

Only two examples will be given (i) for $n < 9$ and (ii) $n > 9$.

Thus to find $(4)_7 \times (8)_7$, $\alpha = 7$, $rr' = 32$ and Table No. II gives the product.

$$(4)_7 \times (8)_7 = 39506164938272$$

Let us find $(4)_{16} \times (8)_{16}$. Here $n = 16 = 9 \times 1 + 7$ giving $k = 1$ and $\alpha = 7$. Arguments $\alpha = 7$ and $rr' = 32$ give 39506164938272. Therefore R = 2 and L = 3950616493827. For argument $rr' = 32$, Table No. III gives (lgr) and (Rgr) as

$$395061728 \text{ and } 160493827$$

respectively. Substitution in the formula gives the product as

$$\underline{395061728} \underline{3950616493827} \underline{160493827} \underline{2}$$

*X. Product $(r)_n \times (r')_n$ when rr' is a multiple of 10;—*The cases that come under this head are only four. (i) $(5)_n \times (2)_n$, (ii) $(5)_n \times (4)_n$, (iii) $(5)_n \times (6)_n$ and (iv) $(5)_n \times (8)_n$. These may be reduced to (i) $(1)_n^2 \times 10$, (ii) $(2)_n \times (1)_n \times 10$, (iii) $(3)_n \times (1)_n \times 10$ and (iv) $(4)_n \times (1)_n \times 10$.

Except for the factor 10, these have been already dealt with in previous sections. It remain only to put a zero at the end in order to obtain a complete product.

*XI. Some remarks:—*A reference to my article on Demlo Numbers pp. 11 to 18 of B. U. Journal of Nov. 1938 will show that the products discussed here are the products of two linear Demlo numbers. A peculiarity in the discussion may be noted *viz.* that the discussion naturally fell into four subdivisions depending upon rr' being multiple of 9 or 3, 6, or 10 or otherwise. This preferential behaviour actuated me to subdivide the Demlo numbers as male, female and neutral.

A theoretical algebraical discussion of the calculation of these values of L, R, K, α , (lgr) (Rgr) will find its place in the collected properties of Demlo Numbers and will form a basis of some wonderful properties of numbers mysteriously ascribed to these by ancient philosophers and mathematicians.

TABLE NO. II.

rr'	$\alpha=1$	$\alpha=2$	$\alpha=3$	$\alpha=4$	$\alpha=5$	$\alpha=6$
1	1	121	12321	1231321	123454321	12345654321
2	2	242	24642	2468642	246908612	24691308642
4	4	484	49284	4937284	493817284	49382617284
5	5	605	61605	6171605	617271605	61728271605
7	7	847	86247	8640247	864180247	86419580247
8	8	968	98568	9874568	987634568	98765234568
14	14	1694	172494	17280494	1728360494	172838060494
16	16	1936	197136	19749136	1975269136	197530469136
25	25	3025	308025	30858025	3086358025	308641358025
28	28	3388	344988	34560988	3456720988	345678320988
32	32	3872	394272	39498272	3950538272	395060938272
35	35	4235	431235	43201235	4320901235	432097901235
49	49	5929	603729	60481729	6049261729	604937061729
56	56	6776	689976	69121976	6913441976	691356641976
64	64	7744	788544	78996544	7901076544	790121876544

rr'	$\alpha=7$	$\alpha=8$	$\alpha=9$
1	1234567654321	123456787654321	12345678987654321
2	2469135308642	246913575308642	24691357975308642
4	4938270617284	493827150617284	49382715950617284
5	6172838271605	617283938271605	61728394938271605
7	8641973580247	864197513580247	86419752913580247
8	9876541234568	987654301234568	98765431901234568
14	17283947160494	1728395027160494	172839505827160494
16	19753582469136	1975308602469136	197530863802469136
25	30864191358025	30864196919358025	308641974691358025
28	34567894320988	3456790054320988	345679011654320988
32	39506164938272	3950617204938272	395061727604938272
35	43209867901235	4320987567901235	432098764567901235
49	~~604~~ 93815061729	6049382595061729	604938270395061729
56	69135788641976	6913580108641976	691358023308641976
64	79012329876544	7901234409876544	790123455209876544

TABLE NO. III

rr'	(lgr)	(Rgr)
1	123456790	098765432
2	246913580	197530864
4	493827160	395061728
5	617283950	493827160
7	864197530	691358024
8	987654320	790123456
14	172839506	382716049
16	197530864	580246913
25	308641975	469135802
28	345679012	765432098
32	395061728	160493827
35	432098765	456790123
49	604938271	839506172
56	691358024	530864197
64	790123456	320987654

A NOTE ON MAXIMA AND MINIMA OF FUNCTIONS OF n VARIABLES.

By

N. R. TRIVEDI.

Take a function of n variables,

$$f(x_1, x_2, \dots, x_n) \quad \dots \quad \dots \quad \dots \quad (1)$$

subject to m conditions,

$$\begin{aligned} \phi_r(x_1, x_2, \dots, x_n) &= 0, & \dots & \quad (2) \\ r &= 1, 2, 3, \dots, m. \quad m < n. \end{aligned}$$

The necessary conditions for an extremum are found by differentiating $f + \lambda_r \phi_r = 0$ (the summation convention being used).

$$\text{Thus } \frac{\partial f}{\partial x_i} dx_i + \lambda_r \frac{\partial \phi_r}{\partial x_i} dx_i = 0 \quad (i=1, 2, \dots, n) \quad \dots \quad \dots \quad (3)$$

and $\therefore$ the conditions are, (n in all)

$$\frac{\partial f}{\partial x_i} + \lambda_r \frac{\partial \phi_r}{\partial x_i} = 0 \quad \dots \quad \dots \quad \dots \quad (4)$$

These n equations together with m equations (2) determine a set of n numbers x_r , say, and m numbers λ_r .

For a maximum at $\bar{x}_r$,

$$df=0, \quad d^2f < 0 \quad \dots \quad \dots \quad (5)$$

Now a maximum for $f=0$ is the same as a maximum for $f + \lambda_r \phi_r = 0$, in virtue of (2). Hence (5) is the same as,

$$df=0, \quad d^2f + \lambda_r d^2\phi_r < 0 \quad \dots \quad \dots \quad \dots \quad (5')$$

Now differentiating the left hand side of (3), we get,

$$\begin{aligned} & \frac{\partial^2 f}{\partial x_i \partial x_j} dx_i dx_j + \lambda_r \frac{\partial^2 \phi_r}{\partial x_i \partial x_j} dx_i dx_j \\ & + \frac{\partial f}{\partial x_i} d^2 x_i + \lambda_r \frac{\partial \phi_r}{\partial x_i} d^2 x_i; \end{aligned}$$

that is,

$$\left(\frac{\partial^2 f}{\partial x_i \partial x_j} + \lambda_r \frac{\partial^2 \phi_r}{\partial x_i \partial x_j} \right) dx_i dx_j \quad \dots \quad \dots \quad (6)$$

since the coefficient of $d^2 x_i$ is zero by (4).

$$\text{Now } \frac{\partial \phi_r}{\partial x_i} dx_i = 0 \quad \therefore \quad \frac{\partial \phi_r}{\partial x_i} dx_i dx_j = 0.$$

Introduce now γ_{rj} , ($r=1, 2, \dots, m$), ($j=1, 2, \dots, n$), $\gamma_{st} = \gamma_{ts}$, $mn - \frac{1}{2}m(m-1)$ arbitrary constants in (6). Thus the inequality in (5)' becomes,

$$\left(\frac{\partial^2 f}{\partial x_i \partial x_j} + \lambda_r \frac{\partial^2 \phi_r}{\partial x_i \partial x_j} + \gamma_{rj} \frac{\partial \phi_r}{\partial x_i} \right) dx_i dx_j < 0 \quad (7).$$

Now choose the γ 's so that, of the n differentials dx_i , m disappear from (7). Suppose $dx_1, dx_2, \dots, dx_m$, so disappear. As the terms involving these are $mn - \frac{1}{2}m(m-1)$ in all, this is in general possible. Hence γ 's are supposed uniquely determined. With these values of γ 's and the previously obtained values of λ 's, we obtain from (7), a quadratic form in $n-m$ differentials

$$dx_{m+1}, dx_{m+2}, \dots, dx_n.$$

$$\text{Say, } A_{ij} dx_i dx_j; \left\{ \begin{array}{l} i=m+1, m+2, \dots, n \\ j=m+1, m+2, \dots, n \end{array} \right\}$$

Now the conditions that this quadratic form should be negative definite as required by (7), are that,

$$A_{m+1, m+1} < 0; \quad \begin{vmatrix} A_{m+1, m+1} & A_{m+1, m+2} \\ A_{m+1, m+2} & A_{m+2, m+2} \end{vmatrix} > 0.$$

$$\dots \quad \dots \quad (-1)^{n-m} \begin{vmatrix} A_{m+1, m+1} & \dots & \dots & A_{n, m+1} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ A_{m+1, n} & \dots & \dots & A_{n, n} \end{vmatrix} > 0.$$

These are $n-m$ in equalities which should be fulfilled for a maximum at $\bar{x}_r$. It may be noted that, though the determination, of the γ 's may present some difficulty in practice, the method given above has the advantage of setting forth the final conditions in a symmetrical form. The current books on analysis, that deal with this topic, give equations (4) (Lagrange's undetermined Multipliers) but none of them, as far as the writer is aware, gives a theoretical sketch of the method to be adopted to complete the discussion of an extremum.

No remarks are necessary regarding a minimum $\bar{x}_r$, for the corresponding changes in the inequalities are obvious. The discussion can be extended to the case of $df=0$, $d^2f=0$ and so on.

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COSMIC RADIATION

By

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[Summary of three lectures given for the University of Bombay]

The discovery of cosmic radiation evolves out of researches towards the beginning of the century on the conductivity of the air. The conductivity of the air as measured by the rate of transfer of charge between two metal surfaces at different potentials essentially depends on the density of ions in the gas, that is, on the number of negatively charged electrons which have been removed from neutral atoms and the number of the remaining fragments of atoms which are therefore positively charged. This ionisation is produced largely by the passage through the gas of charged particles such as electrons and the alpha-rays emitted by radioactive substances. In 1912 Hess took up an ionisation chamber, an instrument for measuring the ionisation, in a balloon and found that the ionisation first decreased with height immediately above the ground, after which it continued to increase markedly to the greatest height then attained. The preliminary decrease has been shown to be due to the decrease of radioactive matter in the air which is known to be greatest near the surface. The subsequent increase was the first definite evidence that part of the ionisation was due to a radiation which came in from outer space and which was hence called cosmic radiation.

These experiments with ionisation chambers in balloons have been carried out recently by Regener and Millikan and their co-workers, the balloon traversing in some cases as much as 98·8% in pressure of the whole atmosphere. In particular, flights have been made by Bowen, Millikan and Neher (1938 Phys. Rev., 53, 855) at different latitudes at the places indicated in Table I.

TABLE I

Place	Madras	San Antonio	Omaha	Saskatoon	
Mag. Latitude	8°	28·5°	51°	60°	
Energy Flow	0·94	1·81	2·25	2·36	10 ⁹ eV./cm ² /sec.
Min. Energies	17	6·7	2·9	1·4	10 ⁹ eV.

The ionisation curves at different latitudes, though not identical, have all essentially the same shape. Starting from sea level the ionisation

increases with height, the increase becoming gradually more rapid, until a maximum is reached at a pressure of about 8 cm. of mercury corresponding roughly to 1/10th of the atmosphere from the top, after which the ionisation falls rapidly (Fig. 1). The area under

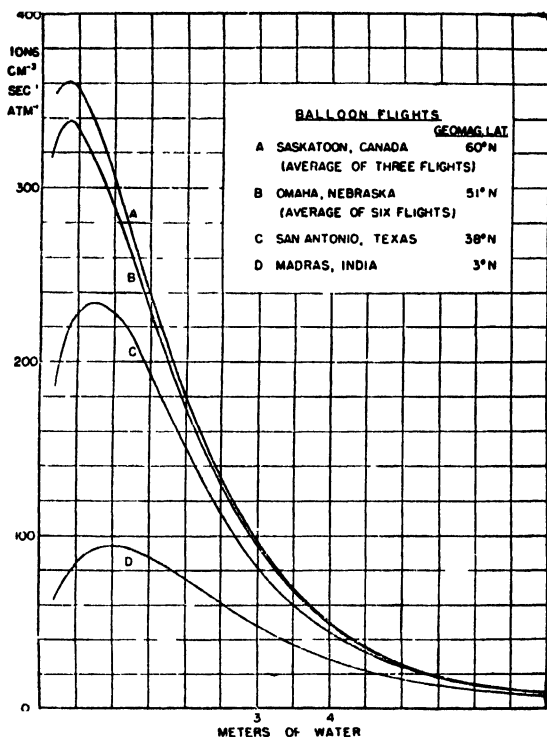


Fig. 1

Results of balloon flights at four different latitudes
(Bowen, Millikan and Neher)

any curve represents the total number of ions produced by the cosmic radiation at the particular place concerned in the process of its absorption in matter. Since an energy of roughly 32 eV. is required on the average for the formation of one ion-pair, we can calculate the total amount of energy which enters in the form of cosmic radiation at the various places. These amounts are indicated in the third row of the table. We see that the total inflow of energy at 50° is approximately 2.4×10^9 eV. per cm.² per sec. which is of the same order as the energy falling on the earth in the form of light from the fixed stars. The table also shows that the amount of cosmic radiation falling on any given

point of the earth's surface is a function of latitude and is greater the nearer we approach the poles. Remembering Strömer's explanation of the distribution of the Aurora which also occur most frequently at high latitudes, we may conclude that the differences of the incoming cosmic radiation at different latitudes are due to the magnetic field of the earth and that therefore the greatest part of the primary cosmic radiation enters the earth in the form of electrically charged particles. Now it has been shown by Strömer (University Observatory, Oslo, Publication No. 10, 1934) that to reach any particular point of the earth a charged particle must possess a minimum amount of energy depending on the latitude. For vertical incidence these minimum energies are given by the simple formula

$$cp = 1.54 \times 10^{10} \cos^4 \Lambda \text{ eV.},$$

where p represents the relativistic momentum of the particle and Λ the magnetic latitude. These minimum energies for vertical incidence are also given in the fourth row of Table I. The

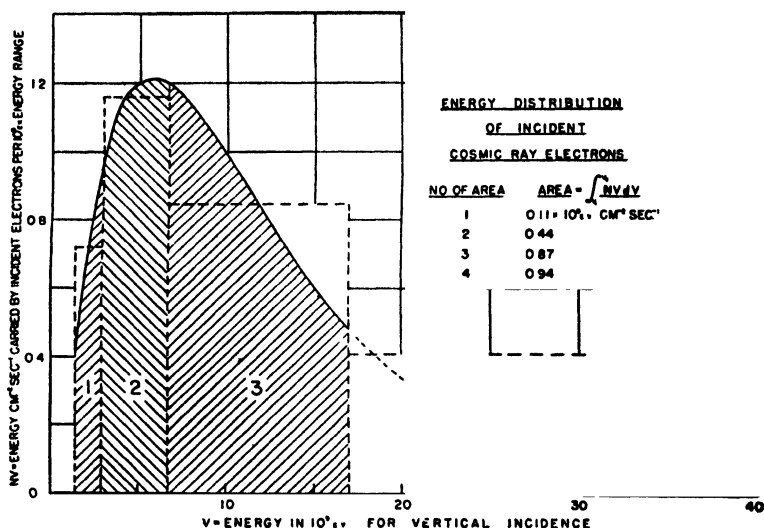


Fig. 2

The areas under each rectangle represent the total energy flow carried by charged particles whose energies lie between the values indicated by the abscissæ, corresponding to the fourth row of Table I. A smooth curve is then drawn so as to enclose the same area below it, and gives the energy spectrum of the charged primary particles. About half of rectangle 4 is due to *uncharged* primaries whose energies however do *not* lie between the limits indicated by the abscissæ. (Bowen, Millikan and Neher.)

difference between the figures in the third row of columns 4 and 5, *viz.* 0.87×10^9 eV. per cm.² per sec., can then only be due to primary particles with energies that lie between the limits 6.7×10^9 eV. and 17×10^9 eV. as shown in the fourth row. In this way, we can construct an energy spectrum of the incoming primary cosmic ray particles (Fig. 2). It should be remembered, however, that the energy which falls at Madras (represented by the area of rectangle 4 in Fig. 2) may be due either to primary particles whose energy is greater than 17×10^9 eV. or to uncharged primary radiation. It shows that at most only one third of the total cosmic radiation could possibly be *uncharged*, and by drawing a smooth curve for the energy spectrum of the charged particles one may conclude that not more than roughly half the energy at Madras *viz.* 0.47×10^9 eV. per cm.² per sec. could be due to *uncharged* primary radiation. The energy spectrum of the primary radiation so derived has a maximum for particles with energies of roughly 5×10^9 eV. It is not yet possible to decide whether the falling off of the spectrum at low energies is an intrinsic property of the radiation in outer space or is merely due to the blocking effect of the Sun's magnetic field. The fact however that uncharged radiation forms but a small fraction (about one sixth) of the total primary cosmic radiation shows in view of the cascade theory to be discussed below that the radiation has not passed through more than about 100 gr. per cm.² of matter in its passage through the universe. In other words, the radiation could at most have travelled a few times round the universe from the time of its production till its arrival on the earth.

At any given place the radiation shows periodic variation with solar or sidereal time of less than 2%, so that it is possible to conclude that an appreciable fraction of the radiation does not come to us from the galactic system, for if it did, we should observe a much greater diurnal variation. Hence an appreciable part cannot be produced continuously in any other galactic system which is essentially like our own. The origin of cosmic radiation therefore still remains unexplained.

Since the ionisation in a gas is produced mainly by the passage of energetic electrically charged particles, the ionisation curves in the atmosphere described above show that the number of particles increases as we go up from sea level, reaches a maximum and then decreases towards the extreme outside of the atmosphere, showing that a rapid multiplication of the number of particles takes place in the passage of cosmic radiation through

the first tenth of the atmosphere followed by a subsequent decrease. This behaviour is what would be expected theoretically if the charged primary radiation consisted of positive or negative electrons. According to theory a fast electron in passing through the field of the nucleus of an atom has a large chance of suffering a small deflection in the course of which it may emit a considerable fraction of its energy in the form of a quantum of radiation. Further, a quantum of radiation of great energy in passing through the field of a nucleus may disappear by the creation of two electrons of positive and negative charge, its energy being transmuted according to Einstein's equation into the kinetic energy and rest mass of the created particles. The consequence of the repeated alternation of these two processes is to give rise as shown by the cascade theory (Carlson and Oppenheimer, 1937, *Phys. Rev.* 51, 220; Bhabha and Heitler, 1937, *Proc. Roy. Soc.* 157, 432) to a great increase in the number of particles when a sufficiently high energy electron traverses matter.

For very high energies the radiation loss per cm. mentioned above may be written in the form (Bethe and Heitler, 1934, *Proc. Roy. Soc. A* ; 146, 83. Bhabha, 1938, *Proc. Roy. Soc. A*, 146, 257).

$$-\left(\frac{dE}{dx}\right)_{rad} = \sigma \frac{Z^2}{137} \left(\frac{e^2}{Mc^2}\right)^2 E \left\{ 4 \log 183 \frac{M}{m} Z^{-1/2} + \frac{2}{9} \right\},$$

where E is the energy of the radiating particle, M its mass, Z the atomic number of the substance, σ the number of atoms per c.c., and e and m the charge and mass of an electron respectively. x is the thickness of the substance traversed in cm. We see from this formula that the radiation loss increases proportionately with the energy of the particle, and is inversely proportional to the square of its mass, so that in effect this process is really important only for electrons and is small for particles of heavier mass. This formula has been experimentally verified for electrons by Blackett and Wilson (1937, *Proc. Roy. Soc. A*, 160, 304; Wilson 1938, *Proc. Roy. Soc.* 166, 482) upto energies of 2×10^8 eV. Cascade processes are therefore only important for electrons, and by taking

$$x_0 = 1/a \frac{\sigma Z^2}{137} \left(\frac{e^2}{mc^2}\right)^2$$

as the unit of length, where a is numerical factor equal to 20 in lead and 23 in air, we can treat all substances alike (Bhabha and Heitler, l.c.), with this difference that the thickness of the substance is now to be measured in the above units of length. These units of length for different substances are given in Table II.

TABLE II

Substance	Lead	Iron	Aluminium	Water	Air
X_0	0.4 cm.	1.4 cm.	7.8 cm.	34 cm.	275 m.
$E_c 10^7 \text{ eV.}$	1	3	6	15	15

The formula for radiation loss may then be written

$$-\left(\frac{dE}{dt}\right)_{rad} = E \log 2,$$

t being the thickness x/x_0 of the substance in the above units. The solution of this equation is

$$E = E_0 2^{-t},$$

E_0 being the initial energy. In other words, in travelling a distance of one unit, the electron on the average loses half of its energy, emitting a number of quanta of comparable energy of the order 1. Counting a quantum of radiation as a particle for the moment, it means that the number of particles is a little more than

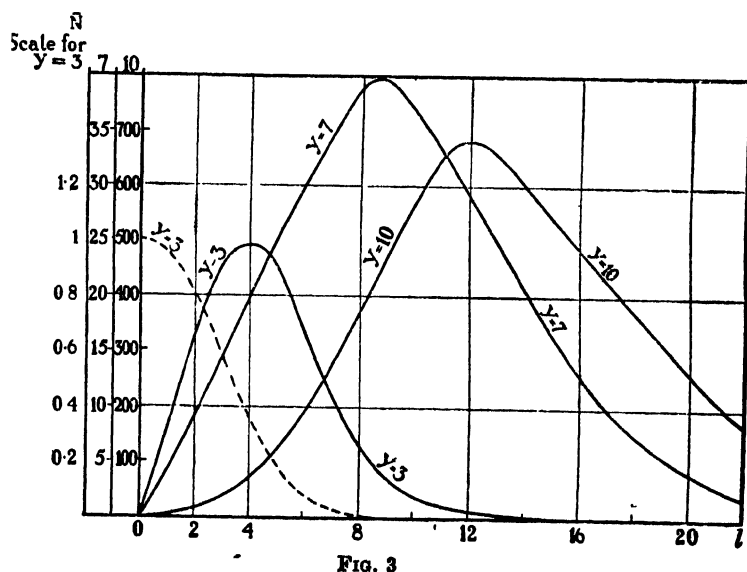


FIG. 3

The ordinates represent the number of electrons or positrons, the total number of charged particles being just double this. The abscissa is the thickness traversed in the units of length x_0 defined in Table II. Here $y \equiv \log_2 E_0/E_c$. (Bhabha and Heitler)

doubled after travelling a distance of one unit. The chance that the quantum of radiation may create a pair is also 0.6 per unit of length, so that due to this process also the number of particles is doubled in approximately one unit of distance traversed. Thus the number of particles would increase very crudely as 2^t until the mean energy has fallen so low that they are absorbed by ionisation as we shall show below. The critical energy E_c at which this happens depends on the atomic number of the substance. The more exact theoretical curves are given in Fig. 3 for different values of $y \equiv \log E_0/E_c$.

I now turn to the rate of loss of energy by ionisation which is given by the formula of Bloch

$$-\left(\frac{dE}{dx}\right)_{ion} = 2\pi\sigma Z \left(\frac{e^2}{mc^2}\right)^2 \frac{mc^2}{\beta^2} \left[\log \frac{mc^2\beta^2 W}{(1-\beta^2)I^2 Z^2} + (1-\beta^2) \right],$$

where $\beta = v/c$, v being the velocity of the particle, $I = 13.5$ eV. and W is the maximum energy transferable to an electron in a free collision. This expression increases rapidly when β is appreciably less than 1, as has been amply confirmed by experiment. It has a minimum for $\beta = 0.97$ after which it increases logarithmically with the energy. The minimum and the logarithmic increase have recently been confirmed upto energies of 3×10^7 eV. by Corson and Brode (Phys. Rev. 1938, 53, 773). The ratio of the radiation loss to the ionisation loss is therefore approximately (Bethe and Heitler l. c.)

$$\frac{-\left(\frac{dE}{dx}\right)_{rad}}{-\left(\frac{dE}{dx}\right)_{ion}} \sim \frac{ZE}{1600mc^2}.$$

We may then define an energy E_c at which this ratio is unity, so that above this energy the radiation loss predominates, and below it the ionisation loss. Hence we have

$$-\left(\frac{dE}{dt}\right)_{ion} = -\left(\frac{dE}{dt}\right)_{rad} = E_c \log 2.$$

so that an electron whose energy has fallen as low as the critical energy is stopped after travelling a distance of 1.4 units by the ionisation loss alone. The critical energies for different substances are given in Table II.

Thus from the point of view of cascade processes an electron may be regarded as stopped the moment its energy falls to E_c , and it can be shown (Bhabha and Heitler l. c.) that the maximum number of charged particles N_m produced by an electron of initial

energy E_0 in travelling through a sufficiently thick layer of matter is given by

$$N_n = 0.12 \left(\frac{E_0}{E_c} \right)^{0.93}$$

showing that the initial energy of the electron is roughly speaking divided between N_n particles all of the critical energy E_c . Similarly it may be shown that the range of a cascade process due to an electron of an initial energy E_0 i.e. the distance after which there is only approximately one electron left is given by the formula (Landau & Rumer, 1938, Proc. Roy. Soc. A, 166, 213).

$$t_0 = 3.8 \log \frac{E_0}{E_c}$$

The initial energy required for a cascade process to penetrate the atmosphere ($t=30$) is according to this formula 3.6×10^{11} eV. showing that there is already a discrepancy with the results of Bowen, Millikan and Neher (1937, Phys. Rev. 52, 80) according to which particles of less than 17×10^9 eV. can make their effects felt at sea level. It also shows that no electron of reasonable energy will make its effect felt through more than about 12 cm. of lead ($t=30$).

These cascade processes are also the explanation of the showers photographed in Wilson chambers at sea level, originally by Blackett and Occhialini (1933, Proc. Roy. Soc. A, 139, 699) and recently by Anderson and Neddermeyer (1936, Phys. Rev. 50, 263), and Street, Woodward, and Stevenson. In these photographs one sees one or more particles in the top of the chamber entering a plate of lead or some other metal put across the middle of the chamber, whereas far more positive and negative particles are seen to emerge from the bottom of the plate. The simultaneous appearance of so many high energy particles which in some cases may number several hundreds is called a shower. Fig. 4 shows a photograph of a typical shower. Moreover the number of showers produced in plates of different thicknesses can be measured by coincidences between a number of counters put below the plate, and gives a curve for the number of showers as function of the thickness of the plate, which has a characteristic shape first found by Rossi (1933, Z. Phys. 82, 151). The shape is similar to the ionisation curve in the atmosphere discussed above, the number of showers increasing with the thickness of the plate till a maximum is reached (at about 1.6 cm. for lead) after which the number of showers decreases. The explanation of this curve is exactly the same as the explanation of the corresponding curve

in the atmosphere and is due to the cascade multiplication of the number of particles, with this difference that the unit of length in lead is only 0.4 cm. instead of 275 m, as in air.

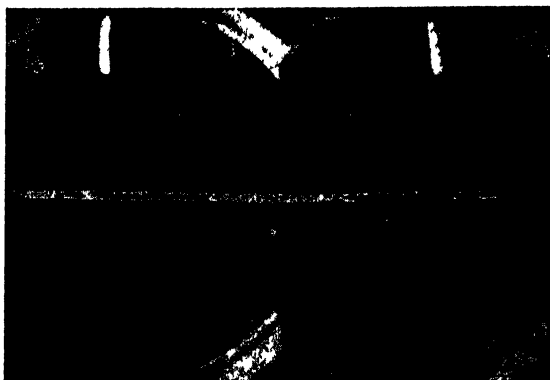


Fig. 4.

A photograph of a shower by Anderson & Neddermeyer, showing multiplication of the number of particles in the 0.35 cm. lead plate which runs across the middle of the chamber.

Measurements of the absorption of cosmic radiation have also been carried out to great depths of water by Clay, Regener and others. The latest experiments of Ehmert (1937, *Z Phys*, 106, 751) show that the number of coincidences $N(l)$ between three counters in a vertical plane can be represented very well by the formula.

$$N(l) = \frac{659}{l^{1.56}} \text{ coinc./min.} \quad 13 \leq l \leq 43 \text{ m.}$$

$$N(l) = \frac{2170}{l^{1.87}} \quad \text{"} \quad \text{"} \quad 43 \leq l \leq 243 \text{ m.}$$

l being the thickness from the top of the atmosphere in meters water equivalent. A measurement by Barnothy and Forro in a mine at a depth of 732m. water equivalent shows that the same formula holds even upto these depths. It is impossible for any cascade process to penetrate to such enormous depths, and we have here clear evidence that this penetration is due to the presence of particles which are neither electrons nor gamma-rays.

" That we have to do in cosmic radiation with two types of particles of different penetrating power was first put in evidence by Auger and his co-workers (1936, *J. Phys. Radium*, 7, 58). They measured the decrease in the number of coincidences between two

or three counters placed in a vertical plane by the interposition of increasing thicknesses of lead, thus measuring in effect the number of particles capable of vertically traversing the thicknesses of lead concerned. It was found that 10 cm. of lead reduced the number of coincidences to about 75% of the initial value without lead, whereas the addition of a further 90 c.m. of lead did not reduce the number of coincidences to less than 30% of the initial value. Following Auger it has been customary to describe the group of particles absorbed in the first 10 cm. of lead as the soft group, whereas the group which penetrates more than a meter of lead is described as the hard group. The ratio of soft to hard group has similarly been measured by Auger and Ehmert at different points above and below sea level and the results are given in Table III.

TABLE III

Altitude	Jung Fran	Sea Level	Below Sea level			
			12 m.	30 m.	75 m.	All depths
Soft Component Total Radiation	40%	25%	9%	10%	2%	15-20%
			Results of Auger and co-workers			Results of Ehmert.

These results show that after 12m. of water equivalent below sea level the soft component always constitutes between 9 and 15% of the total radiation* and therefore leads one to suspect that it is produced by the hard component with which it is in equilibrium. As has been mentioned earlier, the radiation loss varies inversely as the square of the mass, so that the particles comprising the hard group must have masses considerably greater than that of the electron. The dominating process is then the following:—The penetrating particle in its passage through matter occasionally makes a very hard collision with an atomic electron, communicating to it a considerable fraction of its energy. This electron then starts a cascade process and the number of electrons multiplies. In this way we get a soft com-

* There is some disagreement here between the results of different workers.

ponent consisting of electrons in equilibrium with the penetrating particles, and its amount depends on the mass M and energy of the penetrating particles. The percentage of the soft component to be expected theoretically (Bhabha, 1938, *Proc. Roy. Soc.* 164, 257) is 14–31% for $M \sim 10 m$, and 6–15% for $M \sim 100 m$, and allows one to conclude that the mass of the penetrating particle is of the order of a few hundred times the electron mass.

About half a dozen Wilson chamber photographs have been taken in recent years by various authors, in particular by Williams and Pickup (1938, *Nature*, 141, 684) in which the heavy particle has been slow enough for one to estimate its mass from a measurement of the curvature of its path in a known magnetic field and the density of the ionisation along its track. The mass of the heavy electron,* as it is called, may be put between the limits 200 ± 50 times the mass of the electron, in agreement with what has been mentioned above.

A particle of this description had already been required by a theory tentatively put forward by Yukawa (1935, *Proc. Phys. Math. Soc. Japan*, 17, 48) to describe the nature of nuclear forces. I now proceed to deal with the underlying ideas of this theory. The vast amount of experiment which has been done on the properties of nuclei shows that these are to be considered as made up of protons and neutrons only and that the forces between any two nuclear particles, that is either two protons or two neutrons or a proton and a neutron are as far as we can tell the same (allowing for the Pauli principle by which like particles can only be in anti-symmetrical states). Further, the force between a proton and a neutron is partly of an "exchange" character, that is, whenever an interaction takes place the proton changes into a neutron and the neutron into a proton. All these forces have this in common that the potential energy is very great when the distance between the particles is of the order of the "classical radius" of the electron e^2/mc^2 or less, and it falls rapidly to zero beyond this distance, in contrast with the electrostatic energy between two charges which follows the Coulomb law and falls away inversely as their separation. The idea of action at a distance is foreign to modern physics and it is the custom to suppose that the action of one particle on another is exerted through the intermediary of a field following well defined mathematical laws. In the case of electrical forces the field is the ordinary electromagnetic field

* It has now come to be known as the meson or mesotron.

obeying the Maxwell equations, and the electrostatic potential ϕ of this theory satisfies the d'Alembert-Laplace equation

$$\left(c^2 \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2} \right) \phi = \rho,$$

ρ being the electric density, the solution of which shows at once that the potential due to a point charge e is

$$\phi = \frac{1}{4\pi} \frac{e}{r},$$

which leads at once to the Coulomb force between the two charges. In order to explain the short range character of nuclear forces Yukawa assumed that the corresponding potential responsible for nuclear interactions obeys the slightly different equation

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2} + \lambda^2 \right) \phi = g\sigma$$

where σ is the density of protons and neutrons, and λ and g are arbitrary constants. The solution of this equation shows at once that the nuclear potential at a distance r from a proton or a neutron is given by

$$\frac{g}{4\pi} \frac{e^{-\lambda r}}{r},$$

which therefore accounts for the characteristic short range of nuclear forces.

In quantum mechanics the energy E and momentum p may be represented in a suitable system by the operators

$$E = i\hbar \frac{\partial}{\partial t}; \quad p_x = -i\hbar \frac{\partial}{\partial x}; \quad p_y = -i\hbar \frac{\partial}{\partial y}; \quad p_z = -i\hbar \frac{\partial}{\partial z},$$

$\hbar$ being Planck's constant divided by 2π and i the imaginary root of -1 . Using these relations the equation for the nuclear potential may be written in the symbolic form

$$\left(-\frac{E^2}{c^2} + p_x^2 + p_y^2 + p_z^2 + \lambda^2 \hbar^2 \right) \phi = 0,$$

But this is just the equation for the wave function of a particle of energy E , momentum p , and mass $M = \frac{\lambda\hbar}{c}$. Since the nuclear forces have a range $e^2/mc^2\gamma$, where γ is approximately 2, it follows that

$$M = \frac{\lambda\hbar}{c} = \frac{\gamma mc^2\hbar}{e^2 c} = 137\gamma m \sim 250m,$$

so that the particle the virtual emission and absorption of which is the cause of nuclear interactions has to be a particle of a mass some

GRAVITATION

By

PROFESSOR V. V. NARLIKAR,

INTRODUCTION

I am grateful to the Syndics of the Bombay University for the distinction that they have conferred upon me by inviting me to give a course of four lectures on "Gravitation". Six years ago, when I was honoured by another invitation, I spoke on the same subject but the lectures* published on that occasion are vastly different from the present series. During the last few years Eddington, Milne, Robertson and others have broken new ground in the field and their researches mark a new epoch in our understanding of gravitation. New observations have supplanted old theories and new theories have risen in their stead; new theories have invalidated old interpretations and new ones have commenced to reign; and new interpretations, as they outrun common experience and scientific belief, have been demanding more observations. To give a synoptic view of all these is well nigh impossible as opinion is sharply divided on crucial questions. Indeed, science presents the curious spectacle of workers who agree by convention on fundamental issues and differ, as a rule, on incidental ones. It is believed to be the business of a philosophy of science to justify the basic conventions in the light of man's rationalized experience *in toto* although pioneers, like Newton and Galileo rested their philosophy on theological conceptions of God, Freedom and Immortality.† Philosophies which radically differ from each other cannot support the same superstructure of science. In the course of this treatment, therefore, several conflicting philosophies will appear within our view. Again, the mathematical method is so general on one hand and, on the other, the empirical data are so poor that our conclusions are not usually unequivocal; and a unique and inexorable set of compatible conclusions, which one wishes for is rarely to be had after ploughing through calculations. We are sharply reminded of this when we come to the interpretation of the red-shift of the nebulae and the problem of world-structure.

In the first lecture we explain why the Newtonian theory of gravitation has been abandoned in favour of Einstein's theory and a brief exposition of the latter is given. Several mathematical expositions of general relativity have been published but the difficulties of measurement are usually skipped over in them. In the second lecture the difficulties are considered and the weak points in the logical development of Einstein's theory, which are worthy of attention, are pointed out. Every theory in the field has

* c.f. (17b).

† c.f. (25).

its weak points, but they are often scrutinized and attended to only when discord between theory and observation becomes glaring. Einstein was not the first rebel against Newton's philosophy of space-time: Leibniz and Mach preceded him; but the first successful rebel was Einstein because the technique of experimentation had improved sufficiently by his time to take the astronomers to new places beyond the decimal point. It may be a long time before observations compel us to give up general relativity. Even now it is urged by some that two of the crucial tests are not satisfied by Einstein's theory and that facts call for a new explanation. Although general relativity is considered to be safe from these criticisms it cannot any longer be denied that the theory does not provide a satisfactory solution of the problem of motion of finite bodies. In fact Einstein has been the first to admit it and modify the theory accordingly. Einstein's new relativity forms the subject matter of the third lecture. Every physical theory necessarily contains conceptual as well as empirical elements. The reason of this is not far to seek: in a physical theory such as relativity concrete facts of experience are connected by abstract mathematical relations. Now the main contention of some of the critics against relativity is this: general relativity like any other physical theory is partly conceptual and partly empirical but what ought to be deducible in the theory is empirical and what ought to be empirical in it is conceptual. To be more explicit, the theory ought to deduce from its postulates why, for example, the constant of gravitation has a particular value and it should also leave the freedom to a set of observers to construct their own space and time rather than force a conceptual Riemannian metric on them. Authorities differ on the question as to whether the dynamical manifold must be the same as the metrical manifold of space-time as in general relativity.* It is only if the two manifolds are identical that astronomical observations can decide the curvature of space-time and determine the size and behaviour of the universe as a whole. Lately the problem of world-structure has attracted considerable attention and the methods of general relativity have been extensively used in treating it. In the light of Milne's recent work one is inclined to take the cautious attitude that many of the observed features of world-structure, if not all, can be explained purely kinematically without recourse to a theory of gravitation. If, as an alternative to this, the situations presented by world-structure are considered as gravitational no theory of gravitation can boast a satisfactory formulation until extra-galactic phenomena are incorporated within its framework. Being so important in a study of gravitation the topic of world-structure is taken up in the fourth lecture.

In discussing the different theories of gravitation a church-tower view is taken of certain developments and a few details are subjected to a bird's-eye view. We are more concerned here with the march of underlying ideas than with the proofs of mathematical theorems. Our object is to acquaint the humble research student, pushing on in their line, with the doubts and difficulties that have haunted the minds of the masters. That should

* c.f. (15b) pp. 9-14; (28); also (38b).

account for the lack of the text-book-type lucidity in our mathematical account.

I cannot forget the enthusiasm with which the lectures were delivered and also received. With the same enthusiasm I am sending these lectures to the press although I should have liked some friendly critic to go through the manuscript first. What I owe to the encouragement from my friends, Dr. G. S. Mahajani and several others, is beyond measure. But for the encouragement I would not have been able to accomplish even this little bit. Whether the reader benefits or not by a reading of these lectures the author has certainly found the task of preparing them to his great advantage.

I

1. THE NEWTONIAN THEORY OF GRAVITATION

It is said that when Archimedes sat in his tub modern science was born and that when Newton sat in his orchard modern science came of age. The celebrated falling apple is supposed to have inspired Newton with the great thought of universal gravitation. He could build up a theoretical structure on Galileo's experiments on falling bodies and deduce from his laws Kepler's empirical results of planetary motion. With his three laws of mechanics and the law of gravitation Newton inaugurated the first systematic study of the motions of celestial bodies and of a host of problems in natural philosophy. Science knows no empirical theory which has been as successful in its applications as Newton's theory of gravitation. The problem of lunar motion gave Newton a headache as it seemed hopelessly unmanageable then but thanks to the epoch-making work of Hansen, Delaunay, Hill, Brown and others tables of the moon's motion are available. By means of Newton's theory new planets have been discovered, tides and eclipses are calculated with remarkable accuracy and the spherical shapes and motions of most of the celestial bodies are explained. We have in the theory a rational explanation of the paradox that both the British and the Australians stick to the surface of the earth. The theory has advanced our knowledge of ballistics. In fact the law of gravitation claims such astonishing successes in our neighbourhood and in the skies that it has made us more rational not only in our outlook to questions of science but also in other domains of mental activity.

Thomson and Tait* have stated Newton's law of gravitation as follows :—

"Every particle of matter in the universe attracts every other

* c.f. (30)

particle, with a force whose direction is that of the line joining the two, and whose magnitude is directly as the product of their masses, and inversely as the square of their distance from each other."

In the first instance, therefore, gravitation does mean attraction in conformity with Newton's law. But, as will be shown later, this representation in terms of universal attraction is found to be unsatisfactory in every way and new representations to account for the same and cognate material phenomena have been proposed. The term, 'gravitation,' does persist even in the new representations although it implies something quite different from attraction.

The law stated above is to be considered along with Newton's laws of mechanics and his several postulates including those of space and time. When the entire system of laws and postulates is critically examined Newton's theory is found to be unacceptable in spite of its many successes.

It is not enough for a physical theory to be logical ; it is not enough for it to account for observed facts : a physical theory ought to be both, logical as well as consonant with results of observation. Probably no physical theory has so far been constructed which can be called logical. We have had physical theories which are mathematical but until mathematics is securely established as a form of logic we cannot say that mathematical physical theories are logical. However, at the present stage of our knowledge, we may safely proceed with the assumption that mathematical physical theories are logical. The history of science knows of several logical theories which have been discarded for not being in agreement with observations. It stands to reason that every logical system need not necessarily find a place in the ordering of our experience. Euclidean geometry constitutes a logical system but our experience may be so ordered that Euclidean results do not fit in with it. It is obvious that a theory which gives accurate results but which is not logical cannot be accepted. For such a theory has no method and there is no guarantee that the predictions of the theory will come out true. To give credence to a theory with internal contradictions is going against the scientist's primitive faith that an order prevails in nature which can be determined by human experience. Lastly, it should be clear that no physical theory, logical though it may be and attended by success, cent percent to-day, will escape being wrecked one day on the rocks of new experience. Because the

postulates and conventions on which a theory is based have always to be modified or altered as our insight into the inner processes of nature goes deeper.

Newton's theory has several weak points of logic. It is also found to disagree with observation. Moreover, the postulates of space and time on which the theory is based are in conflict with our broadened vision of natural phenomena.

Consider first the weak points of the logic of the theory. The empirical element of a theory vitiates its logic. The theory does not explain why masses attract and do not repel, why the constant of gravitation γ has its particular value and why the attraction is inversely proportional to the square of the distance and not the cube. These features are incorporated in the theory because observations demand them or rather because they explain certain observations. It is true that this is not a criticism of the logic of the theory but of the law of gravitation itself which is arbitrarily stated and not deduced from any postulates of sense-data. Newton's postulates regarding absolute space and time have been severely criticized by Leibniz.* The representation of events in terms of an absolute space and a unique time introduces a number of characteristics in the description which are either unobservable or irrelevant. Thus, in the Newtonian scheme of space-time, an object may be at any instant (1) at absolute rest in space, (2) in a state of uniform motion in a straight line or (3) in a state of acceleration. Newton gave a criterion to distinguish the state (3) from either of the other two states but no criterion was furnished to distinguish the state (1) from the state (2). A confession to this effect is found in Newton's first law of motion. This weakness of the Newtonian representation does not persist in special relativity where the distinction between (1) and (2) is shown to be unessential, being due to the special space-time chosen by an observer.

Newton's conception of a uniform flux of time has been justly criticized by Mach. One has to realize that in formulating his postulates Newton was guided by theological considerations. But the latter may lead two religious-minded philosophers to adopt opposite points of view as is illustrated by the controversy between Newton and Leibniz. Suppose, for example, that Newton was right in assuming that there exists an absolute time or calendar, unique for all parts of the universe. Using this calendar one finds

*The reader is referred to the concise but masterly treatment of Weyl (35); also to Mach's 'Mechanics.'

that an outstanding event, say, the creation of the earth took place 10^9 years ago. The question that Leibniz asked was : Why did not God create the earth a year earlier or a year later ? The answer that came from a follower of Newton was that it was God's will to create the earth when it was created ; Leibniz did not find in this a sufficient reason and being a religious person, did not consider it in keeping with the dignity of God to force his will so arbitrarily upon Creation. Modern science takes the same attitude as Leibniz did. Whenever science finds itself in a blind alley or scientists fear that they have touched ' the fingers of God ' a rebel movement is born which forces the march of science on a new highway of reason.

Many, indeed, are the criticisms against the Newtonian concepts of space and time, of an all-pervading mechanical aether, of an infinite velocity of the propagation of gravitation. I shall skip over them and mention the observational evidence against the Newtonian theory.

The perihelion of Mercury has been observed to have a motion of $575''$ per century. The theoretical result was $532''$ per century and so the excess of $43''$ per century could not be accounted for on the Newtonian basis. No tentative hypothesis or modification of Newton's law was found plausible and the position was bad enough to call into question the credentials of Newton's law. It is here that we realize the importance of giving a mathematical backbone to a physical theory. A mathematical proposition may be found to be true in 999 cases or more ; but if it fails in one particular case the proposition must be wrong. It is the infallibility of mathematics and the unfailing loyalty of mathematical conclusions to corresponding data that give a unique status to mathematical law : hence the attempt of the physicist to present all laws of nature as mathematical laws.

The last blow to Newton's theory came from the Michelson-Morley experiment. The results of the experiment led to two alternative conclusions ; one clashed with man's intuitional belief that the earth under his feet does not enjoy a privileged position in the universe while the other conclusion clashed with the scientist's theory of space, time and matter. The scientist as a human being stuck to his intuition and courted the conclusion that ultimately threw the Newtonian theory overboard. This conclusion says that the velocity of light is an absolute constant, being independent of the velocity of the source. We are presented now with a curious situation: the velocity of matter depends on the observer, the velocity of radiation is independent of the

observer. The Newtonian representation was found to be utterly inadequate to account for this curious situation.

Thus the evidence grew against the established ideas of Newton's theory and paved the way to the great revolution in thought heralded by Einstein's earlier writings.* Before I pass on to general relativity I shall refer to a technical matter of some interest.

2. THE CONCEPT OF MASS†

It is well-known that the equality of the inertial and gravitational masses, which is hypothetical in Newton's theory, is an inevitable consequence of the principle of relativity. The inertial mass makes its debut in Newton's laws of motion and the gravitational mass, in the law of gravitation. The kinematical response which a body gives to an external influence is measured by its inertial mass and the gravitational influence that it itself exercises on another tells its gravitational mass. Granted that the inertial mass of a body is numerically the same as its gravitational mass the question is, how are the mass-numbers assigned? Newton's laws of motion throw no light on this question. Following Mach, however, we may regard the first law of motion or the law of inertia not merely as

$$m \frac{du}{dt} = 0, \quad (2.1a)$$

$$\text{but also with} \quad \frac{dm}{dt} = 0, \quad (2.1b)$$

m being the mass-number, u the velocity in a straight line and t , the time variable. When both these equations are valid we can conclude that, in the absence of forces,

$$\frac{d}{dt}(mu) = 0, \quad (2.2)$$

or that the momentum is conserved. The supplement (2.1b) expresses the isolation of the material system m , the constant of integration being determined by the action of the rest of the universe on the isolated body under consideration. That the rest of the universe exercises an influence in this manner on every body is accepted in principle in general relativity and in Milne's

* *c.f.* (12).—This is an early authoritative exposition of relativity. A critical treatment of the observational significance of $g_{\mu\nu}$ will be found in (8).

† *c.f.* (17a); also (17p).

theory as well. Einstein has tried to show even how the inertial mass of a body increases due to the other bodies in the universe moving nearer. We cannot go deeper into the question just here. Suffice it to remark that the concept of mass-number is intimately connected with the space-time distribution of other bodies in the universe. A complete theory of gravitation has to take account of the world-structure. In general relativity a formulation of gravitation is first given, independent of the world-structure, which is later studied in the light of the theory. Milne, on the other hand, first proceeds to consider the substratum or the smoothed out universe and then tries to account for gravitation.

In the general theory of relativity the two questions (2.1) are combined in the conservation of the four-vector, mv^μ , as given by

$$(mv^\mu)_{;\gamma} v^\gamma = 0 \quad (2.3)$$

where a covariant differentiation of mv^μ is supposed to be performed with respect to x^γ . The quadratic scalar invariant associated with mv^μ is $m^2 v^\mu v_\mu$, that is, $m^2 g^{\mu\gamma} v_\mu v_\gamma$ or m^2 . Hence the equations (2.3) imply the constancy of m .

The only solution of Einstein's field equations for empty space which has spherical symmetry and which is Galilean at infinity is known to be Schwarzschild's. The latter is static and gives a constant mass. This may be construed as meaning, firstly, that the field conditions at infinity permit constant mass-numbers only as in Newton's theory and, secondly, that the energy of an isolated system is necessarily conserved. The constancy of mass-numbers may be treated in Newton's theory as well as in general relativity as an illustration of the principle of energy. A conservation principle is a mathematical expression of the isolation of a physical system.

In an isolated system the numerical value of what is conserved has no significance by itself. Hence the constant in the integral of (2.1b) is immaterial so long as the physical system denoted by m is isolated. But as soon as two or more such systems come near enough so that none can be considered to be isolated the constants become important. The problem of particular values of mass-numbers reduces to the problem of the constant of gravitation; and it is now generally admitted that the value of the latter is conditioned by the world-structure.

An outstanding conclusion of general relativity is that there is no essential distinction between mass and energy. Energy has mass and mass represents energy. In the Newtonian theory two independent principles of conservation for mass and energy are

stated. In Einstein's theory the principle of the conservation of energy implies the conservation of mass.

Consider now a radiating mass. That a radiating mass and its radiated energy can constitute an isolated system, surrounded by a flat space-time, has not yet been shown in general relativity. The existence of such an isolated system is necessary for the total energy to be conserved. Whether the total energy of the field is conserved or not it is certain that the mass of a radiating body is not constant. The path traced by a radiating body requires to be carefully determined. When the mass-number is constant the equation implies that the path is a geodesic. What is the path when the mass-number is not constant ?

It may be recalled that the equation of motion of a static or a radiating mass is the same, *viz.*,

$$m \frac{du}{dt} = F, \quad (2.4)$$

in the usual Newtonian notation. In deriving (2.4) use is made of the principle of conservation of momentum. Following the same in the notation of relativity

$$(mv^\mu)_{,\gamma} v^\gamma + \lambda v^\mu = 0 \quad (2.5)$$

where λv^μ is the four-vector for the outgoing radiation per unit time. Hence

$$(mv^\mu)_{,\gamma} v^\gamma v_\mu + \lambda v^\mu v_\mu = 0 \quad (2.6)$$

and, as $v_\mu v^\mu = 1$, it follows that

$$\frac{dm}{ds} + \lambda = 0 \quad (2.7)$$

Substituting for λ in (2.5) we get

$$m(v^\mu)_{,\gamma} v^\gamma = 0 \quad (2.8)$$

which is the analogue of (2.4). Thus a radiating mass also traces a geodesic.

One may as well ask whether the sanction of general relativity is behind the equation (2.5). In natural co-ordinates the equation faithfully represents the Newtonian treatment of the question and one expects, therefore, that the tensor equation may be valid in all co-ordinate systems. In a perfectly general co-ordinate system the field is not regular at the particle m and the differentiation with respect to x^γ cannot be performed. Ignoring the infinities, as Eddington and Clark have done, is an unsatisfactory procedure, not being rigorous mathematically. Einstein and

others have, therefore, launched a new attack on the problem of n bodies according to which motion is given by certain integral conditions of the field. This topic is to be discussed at length in the third lecture and so we may leave it here.

3. THE HYPOTHESES AND POSTULATES IN GENERAL RELATIVITY

The distinction between hypotheses and postulates has been well brought out in the writings of Dingle.* Hypotheses are verifiable while postulates are not. The major hypotheses and postulates in general relativity are the following:—

(A) Events are described with reference to a Riemannian metric of space time,

$$ds^2 = g_{\alpha\beta} dx^\alpha dx^\beta \quad \alpha, \beta = 1, 2, 3, 4 \quad (3.1)$$

(B) Free particles trace geodesics in the space-time field.

(C) Light rays trace null-geodesics, *i.e.* those for which $ds=0$.

(D) The space-time at great distances from a material distribution is approximately Galilean, the line-element taking in the limit a form, equivalent to

$$ds^2 = -dx^2 - dy^2 - dz^2 + c^2 dt^2, \quad (3.2)$$

where c is the velocity of the light.

(E) The principle of equivalence: in a neighbourhood of any point of the field the line-element can be transformed into the Galilean form (3.2).

(F) Gravitation is a field phenomenon, the equations of the field being given by

$$G_{\mu\gamma} - \frac{1}{2} G g_{\mu\gamma} + \lambda g_{\mu\gamma} = -K T_{\mu\gamma} \quad (3.3)$$

In 'empty' space, where $T_{\mu\gamma} = 0$, the equations reduce to

$$G_{\mu\gamma} - \lambda g_{\mu\gamma} = 0 \quad (3.4)$$

(G) The principle of relativity: laws of nature are expressible by equations with the same form and content in all Gaussian co-ordinates. Tensor equations possess the property but non-tensor equations also can represent laws of nature if they are covariant with respect to all Gaussian systems.

(A), (D), (E) and (G) are the postulates while (B), (C) and (F) are the hypotheses. The logic of a theory depends primarily upon

* *c.f.* (2), p. 166.

the postulates and the phenomenological success upon the hypotheses. It is obvious that a theory which is independent of a hypothesis and based mainly on postulates attains the status of pure mathematics; at any rate as it makes no contact with reality, it cannot be a physical theory. The conclusions of a physical theory do not have a generality outside the fundamental concepts which appear in the postulates. Hence a physical theory owes to the generality of its postulates for its inner strength and to the plausibility of its hypotheses for its success.

The relativist believes in an objective world governed by laws of nature. These laws become manifest to us through the events happening in the world if recorded by an observer. The observational data accumulated by an observer contain certain features peculiar to him and a criterion is therefore needed by means of which the subjective element appearing in the data is removed and the natural law is revealed. This criterion is furnished by the postulate (G). In the Newtonian scheme there was no such criterion to distinguish a natural law from a subjective description of events, furnished by the theory itself. Theology and the intuitional authority of pioneers decided what was a natural law and what was not. The history of the principles of Newtonian mechanics bears out this remark. It was Hagel who argued that it was futile to look for new planets, when seven were already known, as God could not have created any but seven planets: for the number seven was supposed to be the most perfect number. When Kepler announced that the planets move about the sun in ellipses he committed the sin of contradicting theology according to which planets must move in circles 'because circles are perfect figures'.

That a subjective element enters in the description of the same set of events becomes obvious when we compare the records of two separated observers in relative motion. Complications are caused by the finiteness and absolute nature of the velocity of light which plays the part of a messenger. A simple illustration of the nature of complication is provided by the fields of causation of two observers in a state of relative motion. Once we are convinced that our descriptions are vitiated by a subjective element the need of a criterion becomes obvious to sift, for a law of nature, the evidence of any number of conceptual observers in different situations. The postulate (G) meets the case splendidly; it is indeed a mathematical formulation of the very general doctrine of relativity according to which all observers in relative motion claim an equal status for their records of observations

and agree in their descriptions of laws of nature. To explain gravitation as a law of nature, in the general terms of the doctrine of relativity, is a great advance in our understanding of physics and this fact will always be appreciated whether the current mathematical exposition of relativity stands the test of time or not.

Newton arbitrarily imposed a particular structure on the amorphous space-time continuum. His own reasons for this particular step were theological and they do not satisfy us. Let us now examine the reasons why Einstein has formulated the postulate (A). The concepts of extension and duration play a fundamental part in our interpretation of experience. Our space-time must, therefore, have a metric giving both the spatial extension and the duration of two events. Only four co-ordinates are chosen, three for space and one for time. The metric is indefinite so that real and imaginary values of ds bring out the distinction between extension and duration while $ds=0$ gives simultaneous events. Einstein's firm conviction that gravitation can be explained as a field phenomenon by differential equations of the second order led him to assume that the metric is Riemannian. Undoubtedly Einstein was very much influenced by the success of Maxwell's field theory.

The Riemannian metric as given by (A) involves ten unknown functions $g_{\mu\gamma}$. If a law of nature is to be expressed in terms of $g_{\mu\gamma}$ it follows from the postulate (G) that there must be a fourfold freedom of the co-ordinate system. This implies that four of the ten $g_{\mu\gamma}$ must be undetermined or arbitrary. The question now arises, how are the remaining $g_{\mu\gamma}$ to be determined in a gravitational situation?

The equality of inertial and gravitational masses can be explained if we take the metrical space-time structure to be the same as the dynamical structure. Moreover, the principle of relativity, as expressed by the postulate (G), drives one to the conclusion that there is no objective reality about the distinction between the state of rest, the state of rectilinear uniform motion and the state of acceleration of a body. This fact is emphasized by stating explicitly the principle of equivalence as an independent postulate (E). By virtue of the postulate an observer is supposed to be able to order his motion so that the phenomena in his own neighbourhood are free from gravitation. These are the reasons which lead one to identify the metrical structure with the dynamical structure and an important consequence of it is the relationship between mass and energy referred to above.

What is meant by the dynamical structure of space-time can be made clearer by reference to an old theory. Democritus suggested as an explanation of the vertical fall of unsupported bodies that space has a direction from top to bottom along which free bodies move. In general relativity empirical evidence of the dynamical structure comes from the hypotheses (B) and (C). It is the geodesics or the 'straight lines' that tell us the structure.

Once it is granted that space-time has a variable structure one wants to know what is responsible for it. We learn from the hypothesis (F) that there is an interaction between matter and the space-time field. It is controlled by the boundary condition (D) to ensure the uniqueness of mathematical solutions and the conservation of energy.

In the present representation gravitation appears as action and reaction between matter and the space-time field. The energy of matter (which includes radiation also) is represented by the tensor $T_{\mu\nu}$. This is a very tentative procedure with unsatisfactory features which will be mentioned later.

We are accustomed to think of action and reaction between two bulks of matter and it is probably not right to talk of action and reaction between dissimilars like matter and space-time. The form of the equation (3.3) may be interpreted as a stress-strain relationship, the stresses being due to the matter and the strains appearing in the structure of space-time. In certain expositions (3.3) is looked upon as a definition of matter in term of space-time curvatures.

4. SOME POINTS IN THE METHOD OF GENERAL RELATIVITY

An attempt has been made to show that the hypothesis (B) is implied in (F). As a result of the identities

$$(G^{\psi} - \frac{1}{2}Gg^{\psi\psi})_{,\psi} = 0 \quad (4.1)$$

we get from (3.3) four equations, viz.,

$$(KT^{\psi} + \lambda g^{\psi\psi})_{,\psi} = 0 \quad (4.2)$$

These equations are of a hydrodynamical character and they are valid for a continuous distribution of matter. It is not possible, therefore, to deduce rigorously from them the equations of motion of a discrete particle in free space. Although all relativists do not hold this view Einstein does consider the hypothesis (B) as extraneous and not implicit in the field equations (3.3).

The term λ appearing in (3.4) must be a constant; otherwise the identities (4.1) are not satisfied. The constant is so small that

it does not affect the questions relating to an isolated and finite distribution of matter. Only in the problems of world-structure it could play a significant part. λ is therefore known as the cosmical constant. The object* of introducing λ was to get over a difficulty raised by the postulate (D) and account for the smallness of the velocities of stars in space. The boundary condition in the postulate (D) says

$$R_{hijk}=0, \quad (4.3)$$

which are twenty conditions, only sixteen being independent. Moreover, the tensor used in (4.3) is different from the tensor $G_{ij}(=g^{hk}R_{hijk})$ in terms of which the gravitational equations are written. The smallness of the velocities of stars in the Galaxy compared to that of light suggests further that $g_{44}=1$, approximately. Mach's idea that the inertia of a body is conditioned by the other bodies in the universe can be incorporated into relativity only by assuming that the space-time of the universe is decided by the matter in it. Einstein believed that all these difficulties can be removed only by introducing the cosmical term λ . A sequel to this was the discovery of the world-models known as Einstein's and de Sitter's. A later investigation by Friedmann showed that the difficulties of an infinite universe disappear if a non-static world-model is adopted. The constant λ is no longer necessary because a non-static model is furnished by Einstein's original equations; the term was therefore put equal to zero by Einstein, in 1932. Eddington has however discovered a new significance of λ and also a theory has been advanced by him connecting λ with other fundamental constants of physics. As we will see later there is a logical weakness in the relativistic theory of measurement by a rod. According to Eddington the cosmical constant must be necessarily non-zero if the weak point in the theory is to be removed. The logical weakness in question is admitted on all hands but Eddington's attempt to remove it is not considered to be successful.

Let us examine the set of equations (3.4), viz.,

$$G_{ij}-\lambda g_{ij}=0, \quad (4.4)$$

describing an unoccupied gravitational field. We retain the cosmical constant λ here, as well as, in later considerations, for the sake of mathematical generality. These equations are ten in number. Are they all independent? If they are all independent their solution will determine all the ten g_{ij} in which case not only the nature of space-time is known but the co-ordinate system of

* c. f. (6 a).

reference turns out to be unique. But, according to the principle of relativity, there must be a four-fold arbitrariness about the co-ordinate system. Hence all the ten g_{ij} should not be fixed by the gravitational equations. Now it can be shown from very general considerations that the necessary degree of freedom about g_{ij} is preserved by the equations (4.4). But the proof of it, which is usually indicated in several mathematical expositions of relativity, I have not been able to follow. It is stated that (4.4) is a system of only six independent equations because of the four identities (4.1). As I could not understand the justification for this statement I considered the analogous case of the twenty equations (4.3). The components are subject to twenty independent identical relations of the form

$$R_{hijk, l} + R_{hikl, j} + R_{hilj, k} = 0 \quad (4.5)$$

known as Bianchi's identities*. It is not obvious how the identities control the independence of the set (4.3). Hence I proceeded to investigate independently the question of independence and my conclusion is that, by their very structure, (4.3) and (4.4) cannot constitute more than sixteen and six independent equations respectively. The proof is as follows:—

$$\text{Let } K_{ab \dots c}^{pq \dots r} = 0 \quad (4.6)$$

be any tensor equation, the tensor being purely a function of g_{ij} and its first n derivatives with respect to x^α . Let one solution of the set of equations be $g_{ij}(x)$. Suppose that we perform the Gaussian transformation

$$x^\alpha = f^\alpha(x') \quad (4.7)$$

then it follows that $g_{\mu\nu}$ transforms into $g'_{\alpha\beta}(x')$ according to

$$g'_{\alpha\beta}(x') = g_{\mu\nu}(f) \frac{\delta f^\mu}{\delta x'^\alpha} \frac{\delta f^\nu}{\delta x'^\beta} \quad (4.8)$$

$g'_{\alpha\beta}(x')$ will certainly satisfy the new set of equations

$$K'_{ab \dots c}^{pq \dots r} = 0 \quad (4.9)$$

Evidently the set of differential equations (4.9) is the same as (4.6) except for the trivial distinction that the independent variables are described as x^α in one and as x'^α in another. Hence $g'_{\alpha\beta}(x)$ also must be a solution of (4.6). In other words, if g_{ij} is a solution of our tensor equation, so is

$$g_{\mu\nu}(f) \frac{\delta f^\mu}{\delta x^\alpha} \frac{\delta f^\nu}{\delta x^\beta} \quad (4.10)$$

In (4.10) there is a four-fold arbitrariness entering through $f^\alpha(x)$.

* c.f. (7), p. 82.

If the tensor in (4.6) has r independent components, four of the equations are satisfied by fixing f^μ while $(r-4)$ equations remain to control g_{ij} . Hence our conclusion that of the equations (4.4) more than six cannot be independent. Similarly, (4.3) does not imply more than sixteen independent equations subject to the further control of the identities (4.5).

The equations (3.4) are ten independent equations as they involve $T_{\mu\gamma}$ which is not entirely a function of g_{ij} and its derivatives. Six of the equations fix g_{ij} leaving a four-fold arbitrariness about them while the remaining four equations must be sufficient to know $T_{\mu\gamma}$. It is evident that we cannot have more than four unknown parameters entering $T_{\mu\gamma}$ if Einstein's equations are to suffice. We will consider fully the particular cause of an isotropic fluid for which

$$T_{\mu\gamma} = (p + \rho)v_\mu v_\gamma - pg_{\mu\gamma} \quad (4.11)$$

in the usual notation. v_μ is a unit vector so that

$$g_{\mu\gamma}v^\mu v^\gamma = 1 \quad (4.12)$$

we will assume a density-pressure relation

$$p = f(\rho). \quad (4.13)$$

That leaves actually only four unknowns in $T_{\mu\gamma}$ besides, of course, g_{ij} . Without any loss of generality we may treat p , v_1 , v_2 , v_3 as the four unknowns.

Incidentally it may be pointed out that both ρ and p are scalar invariants. For

$$T_{\mu\gamma}g^{\mu\gamma} = \rho - 3p \quad (4.14)$$

and

$$T_{\mu\gamma}T^{\mu\gamma} = \rho^2 + 3p^2 \quad (4.15)$$

The full expression of the gravitational equations runs as follows:—

$$G_{ij} - \frac{1}{2}Gg_{ij} + \lambda g_{ij} + k(p + \rho)v_iv_j - Kpg_{ij} = 0 \quad (4.16)$$

p and ρ can be expressed in terms of G and $G_2 = G_{\mu\gamma}G^{\mu\gamma}$ by

$$kp = \lambda + \frac{1}{2}(S - G) \quad (4.17)$$

where

$$S^2 = \frac{1}{2}(4G_2 - G^2) = k^2(p + \rho)^2 \quad (4.18)$$

Hence we may write (4.16) in the form

$$P_{ij} \equiv G_{ij} - \frac{1}{2}Gg_{ij} - \frac{1}{2}Sg_{ij} = -k(p + \rho)v_iv_j. \quad (4.19)$$

when V , is eliminated from the last set of equations we get

$$P_{ii}P_{jj} - P^2_{ij} = 0, \quad (4.20)$$

which are the six differential equations for g_{ij} . Already p has been expressed as a function of g_{ij} in (4.17). It is an easy matter now to get v_1 , v_2 , v_3 as functions of g_{ij} from (4.16). We see

very explicitly here how g_{ij} can be first found out, how four of the unknowns become known as functions of x^α through g_{ij} and how the two remaining unknowns are determined by (4.12) and (4.13).

The observables of the problem may be taken to be p , ρ and ν^μ . We know from the above solution how the values of the observables at an instant control their behaviour in time. The very generality of the space-time systems gives them a very artificial and conceptual character; because each observer is bound to consider his own space-time of experience as real while the co-ordinate frames which other observers might use have only a conceptual significance. Hence in the relativistic treatment of problems the observables are inextricably mixed up with conceptual terms; but the beauty of it is that when the problems are fully solved the conceptual terms drop out and the required information of observables is obtained.

5. ISOTROPY AND GENERAL RELATIVITY

From geometrical considerations of isotropy one is led to the field equations of general relativity. We have to be content with mere directional isotropy as the intrinsic difference between the fourth dimension of time and the other three dimensions of space makes the more general isotropy of orientation impossible. It is indeed this essential difference which makes ds^2 an indefinite form and indicators e_n have to be introduced to distinguish space-like directions from time-like ones.

The directional isotropy of a tensor, at a point P in space, implies that the invariant associated with any direction is the same. The curvature tensor R_{hijk} is isotropic in this sense everywhere as

$$R_{hijk} \lambda_{i_1}{}^i \lambda_{i_1}{}^h \lambda_{i_1}{}^k \lambda_{i_1}{}^j = 0 \quad (5.1)$$

identically, whatever be the vector $\lambda_{i_1}{}^i$. R_{hijk} is not isotropic in the fuller sense, that is, for all orientation ($\lambda_{i_1}{}^i \lambda_{m_1}{}^j$) unless the space-time is one of constant curvature. The question of directional isotropy does not arise about scalars and vectors. The simplest significant case of directional isotropy is provided by a tensor having two suffixes. If L_0 is the invariant of L_{ij} , associated with a direction given by the unit vector $\lambda_{i_1}{}^i$,

$$e L_{ij} \lambda_{i_1}{}^i \lambda_{i_1}{}^j = L_0 \quad (5.2)$$

so that

$$(L_{ij} - L_0 g_{ij}) \lambda_{i_1}{}^i \lambda_{i_1}{}^j = 0 \quad (5.3)$$

Assuming without any loss of generality that L_{ij} is symmetrical,

$$L_{ij} - \frac{1}{4} L g_{ij} = 0 \quad (5.4)$$

$$\text{where } L = L_{ij} g^{ij} = 4L_0 \quad (5.5)$$

It has been proved that the only tensor of two covariant suffixes which is a function of g_{ij} and its derivatives and which does not involve derivatives of an order, higher than two, is of the form $A G_{ij} + B g_{ij}$. Substituting this tensor for L_{ij} we have

$$G_{ij} - \frac{1}{4} G g_{ij} = 0 \quad (5.6)$$

These are Einstein's equations for unoccupied space. Since

$$G^i{}_i - \frac{1}{2} G g^i{}_i = 0, \quad (5.7)$$

identically, we have form (5.6)

$$\frac{\partial G}{\partial x^i} = 0; \quad (5.8)$$

or, G is a constant. If we put

$$G = 4\lambda \quad (5.9)$$

λ is the same as the cosmical constant. The more general equations of gravitation can be similarly introduced through the concept of directional isotropy. For L_{ij} try now the combination

$$\frac{1}{k} (G_{ij} + A g_{ij}) + T_{ij} \quad (5.10)$$

The constant k has appropriate dimensions and its value is empirically determined. The term T_{ij} in the combination is a measure of the stress energy or the energy of matter at any point; the rest is a measure of the local strain energy or the local field energy. We expect the tensor representing the combination to possess the property of directional isotropy. We thus arrive at the equation,

$$(G_{ij} - \frac{1}{2} G g_{ij}) = -k (T_{ij} - \frac{1}{2} T g_{ij}) \quad (5.11)$$

using (5.7) we get

$$k(T^i{}_i)_j = -\frac{\partial \lambda}{\partial x^j}, \quad (5.12)$$

where

$$G = k T + 4\lambda \quad (5.13)$$

If the equation (5.13) is to reduce to (5.9) when $T=0$, λ , as it appears in (5.12) and (5.13), must be constant. Hence we have

$$(T^i{}_i)_j = 0 \quad (5.14)$$

The equation (5.11) can be cast into the well-known form

$$G_{ij} - \frac{1}{2} G g_{ij} + \lambda g_{ij} + k T_{ij} = 0, \quad (5.15)$$

or

$$G_{ij} + k(T_{ij} - \frac{1}{2} T g_{ij}) - \lambda g_{ij} = 0, \quad (5.16)$$

giving

$$\lambda ds^2 = edx^i dx^j [G_{ij} + k(T_{ij} - \frac{1}{2} T g_{ij})] \quad (5.17)$$

The interval between two neighbouring events $\rho(x')$ and $\rho'(x^i + dx^i)$

is ds . There is also a certain stress-strain energy effect associated with ρ and ρ' and measured by

$$edx^i dx^j [G_{ij} + k(T_{ij} - \frac{1}{2}T g_{ij})]^{1/2} \quad (5.18)$$

We understand from (5.17) that the energy effect bears a constant ratio to the interval, *viz.*, $\sqrt{\lambda}$. Here we get an interpretation of the constant λ . The interpretation is not in empirical terms alone. A new concept of an energy effect associated with adjacent events ρ and ρ' is involved in it. If the two events ρ and ρ' are simultaneous so that $ds=0$ the energy effect for $\rho\rho'$ becomes zero.

If gravitation is to be interpreted as a distortion in space-time, of the Riemannian type, we find that the distortion is controlled at each point so as to make the field directionally isotropic everywhere. The structural beauty of Einstein's equations is not obvious when they are expressed in the form (5.15) or (5.16). But the directional isotropy of the field that they represent becomes clear from the equivalent form (5.17) in which dx^i is arbitrary. If the term λ is not equal to zero the interval between two neighbouring events bears the ratio $1 : \sqrt{\lambda}$ to an energy-effect associated with the same events.

We have already shown above that not more than four unknown parameters can enter $T_{\mu\gamma}$. There are four scalar invariant equations to determine the parameters as functions of $g_{\alpha\beta}$ and their derivatives. The equations are connected by λ in an interesting manner.

The gravitational equations (5.15) may be expressed as

$$M_{\mu\gamma} = 0 \quad (5.19)$$

The four scalar invariant equations are

$$M_1 \equiv M_{\mu\gamma} g^{\mu\gamma} = 0 \quad (5.20)$$

$$M_2 \equiv M_{\alpha\beta} M_{pq} g^{\beta p} g^{q\alpha} = 0 \quad (5.21)$$

$$M_3 \equiv M_{\alpha\beta} M_{pq} M_{rs} g^{\beta p} g^{qr} g^{s\alpha} = 0 \quad (5.22)$$

$$M_4 \equiv M_{\alpha\beta} M_{\gamma\delta} M_{pq} M_{rs} g^{\beta\gamma} g^{\delta p} g^{qr} g^{s\alpha} = 0 \quad (5.23)$$

It is found that M_4 is of the form given by

$$M_4 = 4(\lambda^4 + 4A\lambda^3 + 6B\lambda^2 + 4C\lambda + D) \quad (5.24)$$

while

$$\frac{\partial M_4}{\partial \lambda} = 4M_3, \quad \frac{\partial M_3}{\partial \lambda} = 3M_2, \quad \frac{\partial M_2}{\partial \lambda} = 2M_1, \quad \frac{\partial M_1}{\partial \lambda} = 4 \quad (5.25)$$

Therefore the four invariant equations are satisfied if M_4 and its first three derivatives with respect to λ vanish.

We take the liberty of digressing again in connection with λ . When a Ricci-representation is possible for $T_{\mu\gamma}$ we write

$$KT_{\mu\gamma} + \lambda g_{\mu\gamma} = \sum_{h=1}^4 e_h (K\rho_h - \lambda) \lambda_{h1\mu} \lambda_{h1\gamma} \quad (5.26)$$

Hence if

$$4\bar{\rho} = \rho_1 + \rho_2 + \rho_3 + \rho_4$$

it is clear that in the solution of (5.15) $\rho_h - \bar{\rho}$ is independent of λ for $h=1, 2, 3, 4$.

6. GRAVITATION, A LAW OF NATURE

I have often heard people remark: "Whether you believe it or not gravitation exists." What does the remark mean? The remark cannot mean that gravitation as a law of nature must exist whether we believe it or not. Laws of nature are formulated to express our rationalized experience regarding all possible modes of happening in the most general terms. The actual formulation owes its success to the generality of the representation and to our knowledge of the modes of happening. As the representation changes the law of nature presents a different form and content as well. The law of gravitation is one thing in Newton's theory; and quite another in general relativity. Moreover, as our knowledge of gravitational situations advances, a legitimate doubt does arise in the mind as to whether a law of gravitation necessarily exists on some representation, explaining all of them. Hence, when we say that gravitation exists, we do not mean that a law exists on some representation; nor do we mean that the earth attracts an apple as it falls down, nor that the earth and the apple meet because a distorted space-time leaves no other alternative. The remark expresses our conviction that certain experiences which man has had in his neighbourhood from times immemorial will not bear contradiction even to-day. Thus, if a Pharaoh threw a stone vertically upwards and did not move away, his august head was as much exposed to the danger of being hit as the head of a humble experimenter to-day, the relevant circumstances being the same. The experimental truth of this phenomenon is obvious to any person of common sense who may be utterly ignorant of the recondite theories of gravitation. Although it is admitted by everybody that stones thrown vertically upwards descend vertically upon the earth we do not formulate this as a law of nature. Firstly, there is no guarantee that stones thrown with

any velocity, however great, will necessarily return to the earth. Secondly, when stones are not thrown in a vertical direction but with a horizontal velocity, they trace curves the nature of which a law of nature should account for. A law of nature must explain not just one set of experiences but as many different sets as possible. Before Newton enunciated the law of gravitation Galileo's observation that bodies of different sizes and heaviness are subject to the same acceleration when dropped from a height was itself a law of nature. But Newton's law is much more general; it not only accounts for Galileo's observation but a whole empire of facts, unknown to Galileo, is found to be governed by Newton's law. In general relativity when we say that laws of nature are expressible by covariant equations we do not mean that every covariant equation of the theory is a fundamental law of nature. Numerous restricted and particular aspects of a fundamental law appear in the theory in the garb of covariant equations. A law of nature is a rational key to the many mysteries of our experience and it provides an insight into the inner working of nature.

In our search of a wider and more successful law of gravitation we encounter grave difficulties at the outset when we proceed to cast the raw material of sense-experience into an abstract form, suitable for mathematical treatment. If we fail in removing these initial difficulties, our vital conclusions of the theory are bound to bear the marks of our failure. It is necessary, therefore, to examine carefully the foundations of general relativity which we propose doing in the next lecture, although, rather sketchily.

II

7. MILNE'S CRITICISM OF GENERAL RELATIVITY*

"Science," says Whitehead, "Is public fact and private experience." A public fact which has not been privately experienced by anybody does not enter science. The existence of the planet Pluto was not admitted by science until it was inferred from some observed effect. A private experience is certainly essential but it will not be credited by science, even if the experience relates to categories of science, unless it is concerned with a public fact. For example, an observer may perform a scientific experiment and get some results; but if the results are never obtained again, the relevant conditions of the experiment being properly controlled, they are ignored by science. The

**c.f.* 36a, 36b, 36c, 36d, 32, 28 and particularly 15b, pp. 341-47.

results which do not repeat themselves under controlled conditions cannot refer to a public fact.

The important public facts of experience come within the field of private experience through complicated and powerful instruments. The achievements of modern science and the lines on which it is developing now are, in a great measure, due to the great advances made during the last fifty years, in the design and manufacture of optical instruments. The part played by giant telescopes in shaping our theories of world-structure and the revolution in thought following the Michelson-Morley experiment very clearly indicate the importance of instruments.

Instruments are not, however, everything. It is only when the theoretical mind runs ahead of the established facts and anticipates some new results from it that a new experiment is performed. Otherwise experimenting would be, if not for the secondary object of mere training, like taking a small boat and going into the sea in search of a new island. Galileo's celebrated experiment did not require the use of a skilled instrument. But his experiment is to Newton's theory what the Michelson-Morley experiment is to relativity. I suppose Galileo just marched up to the leading tower of Pisa and dropped a number of stones and other heavy objects from its top. If he did not know what he was expecting from the experiment, most probably, he would not have discovered what he did. Far from being called a genius he would have been dubbed a madman. Thus, on the way from private experience to public fact, we recognise the importance of instruments and of the gifted pioneers of science who handle them.

The appearance of a new spot on the sun is a public fact. The dimension of the spot and its time of appearance as recorded by different conceptual observers in relative motion are different. If the time of the first appearance is simultaneous with a certain event according to one observer it will not, in general, be so according to another observer. The time of the event and the dimensions are not the essentials of the appearance of the sunspot as different observers differ in their estimates. According to Milne's exposition of relativity what is of essence in public facts should be describable by a set of functions whose form remains the same for the co-ordinate systems of all observers. But the mathematical formulation of the principle of general relativity says something quite different. According to the latter the functions must remain not only invariant in form but in value also. For example, ds^2 , defined for two neighbouring events has the same

form and value in general and special relativity for all observers while in Milne's theory only the form must be the same. The usual relativistic restriction, according to Milne, is too severe to permit successful applications of the theory.

Milne raises an objection also against the mathematical formulation of the principle of relativity as stated in (G). According to the principle, laws of nature can be expressed by equations covariant with respect to all Gaussian transformations. But some of these transformations are mere tautomerisms, the same physical content being expressed by an alternative set of symbols. These transformations must be distinguished from others which involve passage from one observer to another. Invariance with respect to the latter transformations alone has a physical significance. What Milne particularly objects to is that relativity does not distinguish a mere tautomerism from the other type of transformations. The theory suffers from a cumbrousness of exposition such as might arise if a truth were to be established not only by all possible arguments but in all possible languages at the same time.

The general theory of relativity has dispensed with æther but it has introduced instead a Riemannian space-time. The curvatures of a Riemannian manifold become physical realities just as gravitational attraction is a physical reality to the Newtonian physicist. If one understands the position right nature, according to relativists, prefers a Riemannian space-time to any other. Philosophers have rebelled against this view. Whitehead has argued that the question of metrical structure must be left to intuition and that the dynamical and the metrical structures need not be the same. We cannot subscribe to the view that there exists a unique geometry of the space-time of the world which can be determined by physical measurement and astronomical observation. For physical measurement involves several ill-defined concepts including that of a straight rigid rod and a clock.

We say that the average distance between the earth and the sun is 149×10^9 metres. The statement is considered to be complete if not accurate but, on second thoughts, one finds that it is incomplete and hence ambiguous. In the scientific world such statements are considered precise enough and we will therefore subject this one to a close scrutiny.

Any two metre rods that we take do not agree to an extent that the distance between the earth and the sun will be the same number of units when either rod is used for measurement. It is

necessary therefore to specify which metre rod is used when the distance is stated. Secondly, according to relativity, there is no unique distance between any two points as the space-time is Riemannian. Only a conventional definition of distance can be adopted with reference to a particular co-ordinate system. In order to measure the distance in question we take Schwarzschild's solution in the form

$$ds^2 = -dr^2 \left(1 - \frac{2m}{r}\right)^{-1} - r^2 (d\theta^2 + \sin^2 \theta d\phi^2) + \left(1 - \frac{2m}{r}\right) dt^2 \quad (7.1)$$

The distance is measured along a track in space-time, characterized by constant values of θ , ϕ , t . The track begins on the surface of the sun at $r=r_0$ and ends on the earth at $r=r_1$. The distance l is given by

$$l = \int_{r_0}^{r_1} \left(1 - \frac{2m}{r}\right)^{-1/2} dr \quad (7.2)$$

If we use quasi-co-ordinate we can express the line-element (7.1) at any point of the track in the form

$$ds^2 = -dR^2 - R^2 (d\theta^2 + \sin^2 \theta d\phi^2) + c^2 dt^2, \quad (7.3)$$

then

$$dR = \left(1 - \frac{2m}{r}\right)^{-1/2} dr. \quad (7.4)$$

dR is supposed to be a naturally measured length by means of a rigid rod. Here we see the significance of taking the value of ds^2 invariant and of the principle of equivalence. We learn from (7.4) precisely how a rigid rod of length dR appears to behave in a gravitational field. It is through dR that we can express the distance in metres.

We cannot realize, however, a rigid rod of length dR . However small a rod may be its length is finite. "In mathematics, all phraseology about infinitesimals is merely disguised statement about a class of finites." The first requirement of a rigid rod is that it must be straight. Contortions of curvature are possible for any rigid rod no matter how small. It is necessary further to have a definite notion of straightness with reference to extensive relations if our procedure is to have any meaning. Otherwise there is nothing to choose between two contorted segments with the same end-points, as regards straightness. In geometry a postulate of straightness is constructed. In physics a hypothesis of a straight rigid rod is made so that the results of measurements

are connected by the symbolic abstract relations of the corresponding geometry. The hypothesis is put to test exclusively by private observation.

In physical measurement by a rigid rod some other hypotheses also are involved. The substance of a rigid rod is assumed to undergo no change when it is transported from one place to another. This assumption is contrary to the spirit of relativity according to which events are the basic categories and a hypothesis should be couched in terms of events. Moreover, the rod is assumed to remain congruent to its original self. A metre at one place is supposed to be equal to a metre at another if a standard metre rod is found congruent with the metre at each place. Each comparison may be looked upon as an event; the events themselves are immovable; and the comparison does not prove anything. The relativist assumes therefore that the rod is rigid and that it does not alter its length as it changes its bearing in space-time. The assumption is evidently unsatisfactory and Eddington has tried to remove it by showing that the length of a metre rod bears a constant ratio to the local directed curvature. The gravitational equations for free space are

$$G_{\mu\gamma} - \lambda g_{\mu\gamma} = 0 \quad (7.5)$$

Hence

$$G_{\mu\gamma} v^{\mu} v^{\gamma} = \lambda g_{\mu\gamma} v^{\mu} v^{\gamma} = \lambda \quad (7.6)$$

It may be recalled that $g_{\mu\gamma} v^{\mu} v^{\gamma}$ stands for a unit of the measuring rod. The unit is absolute and unchanged relative to the directed curvature. Eddington* believes that this interpretation of (7.6) is so fundamental that Einstein's theory cannot be logically complete without it. This is his reason for taking a non-zero value of λ . Criticizing Eddington, Russell points out that the process of comparing the rod with the curvature cannot be carried out empirically.

In view of all this Milne has justly abandoned the concept of a rigid rod as undefinable in the formulation of his own theory. The rod and the clock are the ultimate unanalyzable concepts of the theory of relativity. The main difficulties about the clock are two. We cannot test the equality of durations by matching as it is done for stretches and, secondly, an interval that is past cannot be recalled for comparison.

. Again physical time must be distinguished from the observer's subjective time.† The conception of time arises through change.

* c.f. 56, pp. 141-147.

† c.f. (2).

If there are no changes in the objective world, that is, if the physical time is at a standstill, a conceptual observer whose bodily processes are at a dead stop but whose mind and memory are functioning still will be conscious of the passage of time through the succession of his thoughts and awakened memories. Physical time is like an auxiliary variable which is used to describe a succession of events with respect to the order of succession in some fundamental sequence of events. Time is measured by change and change is measured by time. Later on, when we refer to Milne's theory, we will see that the microscopic phenomena reveal one time-scale while the macroscopic ones are explained on an altogether different scale.

It is well-known that historically the Lorentz formulæ were first used in connection with the equations of electrodynamics. The classical interpretation of the formulæ was in terms of absolute space and time and an æther drag. Einstein gave a new interpretation according to which there is no æther drag and no preferential Galilean frame. Now an electrodynamic field is a field of forces the presence of which ought to curve space-time. If the space-time is curved, the Lorentz transformation for a flat space-time cannot be applicable. It is not right to argue that electromagnetic forces do not curve space-time as gravitational forces do ; because mass is recognised to have an electromagnetic origin. Therefore, as Milne has pointed out, there is no justification for using the Lorentz formulæ for a treatment of electrodynamical fields or of any field of forces and accelerations.

"Mathematics" it is said, "makes sense out of nonsense while philosophy reduces sense to nonsense." The functions of mathematics and philosophy are thus complimentary in a physical theory. To transform all sense-data into abstractions, suitable for a mathematical theory, is reducing sense to nonsense. But unless that is done the mathematician cannot make a start. As results verified by observation are given by the treatment mathematics appears to lead from what is nonsense to the layman to some sense. But, one must not be humbugged by mathematics, says Milne. Results which are obtained by very difficult mathematics and which are aesthetically quite satisfactory may be wrong if the philosophical foundations of the theory are not quite sound. A philosophical question is usually solved when the expected answer does not come and a mathematical question is solved when the expected answer does come. The reasons are quite plain. The philosophical question crops up when we have some intuitive or preconceived notion regarding space, time or some other

category which comes into conflict with science. A clear analysis of the question is like unravelling a complicated knot and when that is done the confusion in the mind disappears. In a mathematical question the nature of the answer is known ; mathematics tells us the answer precisely.

After a detailed analysis of the relativistic treatment of space, time and events Milne questions the philosophy of general relativity. He has not gone into the inner technique of the theory which relativists themselves have found faulty at many places. We will go into that in the next section. Relativity must be admitted to be an empirical theory, though it is less empirical than Newton's. Objecting to the relativistic method of the rod and the clock Milne has adopted a new method for defining space and time in empirical terms. It is free from most of the objections cited by Whitehead against the basis of measurement in relativity. Whether one falls in with Milne's philosophy or not the smoothness of his postulates and hypotheses bears a sharp contrast to the arbitrariness of those of Einstein's theory.

8. OTHER OBJECTIONS TO GENERAL RELATIVITY

We have made it sufficiently clear that the principle of relativity itself is found generally acceptable although the exposition of it as given by general relativity has several defects. Einstein himself has raised an objection against the hypothesis (B) better known as the geodesic-postulate. As matter cannot be divorced from motion it is contended that the field equations should give both matter and motion. In other words, (F) should contain (B) and (C) or alternatively (F) should give the equations of motion not necessarily in conformity with (B) and (C). As the three crucial tests of the theory are satisfied because of the geodesic-postulate, if the motion as given by field equations is not in keeping with observation, to the limit of observational accuracy, a serious objection presents itself. Moreover, the principle of equivalence offers a logical generalization of Newton's law of inertia in the geodesic-postulate. In what follows we show that the field equations give both matter and motion and establish further the general result that the world-line traced by every point on the outer surface of a moving body is a geodesic.

, Consider* the inner and outer fields of an isolated spherical mass as given by the line-elements,

* *c.f.* (17n).

$$ds^2 = -\sec^2 x \, dr^2 - r^2(d\theta^2 + \sin^2 \theta d\phi^2) + (A - B \cos x)^2 dt^2, \quad (8.1)$$

$$\text{and } ds^2 = -\left(1 - \frac{2m}{r} - \frac{\lambda r^2}{3}\right)^{-1} dr^2 - r^2(d\theta^2 + \sin^2 \theta d\phi^2) \\ + \left(1 - \frac{2m}{r} - \frac{\lambda r^2}{3}\right) dt^2 \quad (8.2)$$

where $R \sin x = r$.

The boundary conditions that are satisfied at the common surface, $r=r_0$, are two, as usually stated: (i) the boundary pressure $p=0$ and (ii) $g_{ij}=g'_{ij}$, the dash indicating the external field. The boundary conditions in the corresponding problem of Newtonian gravitation suggest that there is one more condition to be satisfied at $r=r_0$; and this is found to be that the laws of mechanics,

$$(T^\gamma_\mu)_\gamma = 0 \quad (8.4)$$

hold good whether we use in (8.4) the three-index symbols for $g_{\mu\gamma}$ or for $g'_{\mu\gamma}$ at the common surface. The new boundary conditions are

$$(T^\gamma_\mu)_\gamma = (\dot{T}^\gamma_\mu)_\gamma = 0 \quad (8.5)$$

In the one-body problem considered above this merely demands

$$\mu_4 \quad \mu_4, \quad \mu=1, 2, 3, 4 \quad (8.6)$$

which is found to be true.

For a perfect fluid for which the condition of continuity holds good in the form

$$[(p+\rho) v^i]_{,i} = 0 \quad (8.7)$$

if, at the boundary, the pressure-gradient is supposed to be negligible compared to the density, (8.7) leads to the equations of the geodesics,

$$(v^i)_j v^j = 0 \quad (8.8)$$

By the new boundary condition, (8.8) are geodesics not only of the inner field but of the outer field also. Thus, at the surface, a fluid traces geodesics in the external field. When a finite fluid mass is of dimensions small enough to be treated as a particle the latter is expected to describe a geodesic. The method, chalked out here for the one-body problem, appears to be the one to be pursued for the solution of the n-body problem.

Whether a solution satisfying all the conditions exists and whether it is unique are problems found to be too difficult for investigation. When the problem of n-bodies is so formulated as

one of boundary-and-field conditions not only the motions under mutual gravitation but also the shapes of bodies as affected by gravitation come within the scope of investigation. The preceding argument shows how the surface points trace geodesics as a result of the boundary conditions.

The above considerations make one fact clear : if the problem of matter and motion is to be solved by means of $T_{\mu\gamma}$ it is necessary to find the appropriate boundary conditions giving a unique solution. We have shown how the geodesic motion of small masses, verified in the case of planets, follows from the field equations and a certain set of boundary conditions, the validity of which will be established, if they are found to imply the uniqueness of the solution. We cannot forget, however, that $T_{\mu\gamma}$ is only tentatively introduced into the theory and that a more rigorous formulation of general relativity should dispense with it. This is what Einstein* wrote in 1921 : " We have seen, indeed, that in a more complete analysis the energy tensor can be regarded only as a provisional means of representing matter. In reality, matter consists of electrically charged particles, and is to be regarded itself as a part, in fact, the principal part of the electromagnetic field. It is only the circumstance that we have not sufficient knowledge of the electromagnetic field of concentrated charges that compels us, to leave undetermined in presenting the theory, the true form of this tensor."

In his later and more recent writings Einstein has pointed out a logical difficulty created by the tensor $T_{\mu\gamma}$. In the theory matter is supposed to be absent where the tensor $T_{\mu\gamma}$ vanishes. But where $T_{\mu\gamma}$ is zero the field energy is not necessarily zero and, as energy has mass, $T_{\mu\gamma}$ is not an effective representation of matter. In this connection Einstein and Infeld† write : " We cannot build physics on the basis of the matter concept alone. But the division into matter and field is, after the recognition of the equivalence of mass and energy, something artificial and not clearly defined. Could we not reject the concept of matter and build a pure field physics ? What impresses our senses as matter is really a great concentration of energy into a comparatively small space. We could regard matter as the regions in space where the field is extremely strong. In this way a new philosophical background could be created. Its final aim would be the

* c.f. (6a), pp. 80-81.

c.f. (6d), pp. 257-258.

explanation of all events in nature by structure laws valid always and everywhere." In this passage is indicated on what lines Einstein would modify the theory of relativity. In the current theory both matter and field enter as realities through $T_{\mu\gamma}$ and $G_{\mu\gamma}$. A more satisfactory theory of gravitation would be a pure field theory explaining matter and motion without the help of a tensor $T_{\mu\gamma}$.

It has not yet been rigorously proved that Einstein's theory reduces to Newton's in the first approximation; and this cannot be said to be done until the problem of n -bodies is solved and the general nature of solutions of Einstein's field equations, subject to the boundary condition (D), is shown to be in keeping with observation. The latter remark is made with Silberstein's* solution of two static mass-centres in view. It has been shown that the solution does not satisfy the boundary condition at infinity. But if the solution were proved to be right it was enough to call forth a revision of field equations because it contradicted observation and Newton's theory.

The dynamical problem of motion is rendered difficult by the appearance of singularities in the field. The field equations are valid only where the field is regular. Einstein expressed even the view that gravitational equations cannot give any information about the motions of particles so long as they are represented by singularities. To launch a new attack on the problem of n -bodies, in the light of this ideology, representative singularities have first to be transformed away. Einstein and Rosen† have shown that the singularity appearing in Schwarzschild's solution, *viz.*,

$$ds^2 = -\left(1 - \frac{2m}{r}\right)^{-1} dr^2 - r^2(d\theta^2 + \sin^2\theta d\phi^2) + \left(1 - \frac{2m}{r}\right) dt^2 \quad (8.9)$$

is removable by the transformation,

$$r - 2m = u^2 \dots\dots\dots (8.10)$$

The result of the transformation is

$$ds^2 = -4(u^2 + 2m)du^2 - (u^2 + 2m)^2(d\theta^2 + \sin^2\theta d\phi^2) + \frac{u^2}{u^2 + 2m} dt^2; \dots\dots\dots (8.11)$$

certainly there is no singularity in the line-element but what has actually been done is that the singularity is transformed from the line-element (8.9) to the transformation (8.10). The Jacobian

* *c.f.* (23) and (6c).

† *c.f.* (6b).

of the transformation is zero at $u=0$. In general relativity only non-singular transformations are allowed so that the Jacobian of the transformation has to be everywhere non-zero and finite within its domain. Moreover, (8.11) is free from a singularity only if m is positive. This was offered as a tentative explanation as to why only positive values of masses are permissible. There is no doubt that a theory of gravitation ought to prove also why masses only attract and do not repel. But we do not believe that a satisfactory proof of this is provided by the above considerations. A theory of gravitation ought to prove also why matter is atomic and explain the electromagnetic origin of mass. Einstein and Rosen have given thought to these questions in their first paper but evidently no progress has been made on these lines. But the question of the field equations giving both matter and motion is solved differently and in an ingenious manner in a joint paper by Einstein, Infeld and Hoffman, which forms the subject of the third lecture.

There are certain problems of which general relativity has not so far been able to provide a solution. One such problem is the field of a radiating mass.* The relativistic field of an isolated radiating mass is worth investigating. No generalization of Schwarzschild's solution exists, with radial symmetry, for a non-static mass. If the principle of energy is to hold good, that is, if the combined energy of matter and field is to be conserved the system must be an isolated material system surrounded by flat space-time. A spherical radiating mass would probably be surrounded by a finite and non-static envelope of radiation with radial symmetry. This would be surrounded by a radial field of gravitational energy becoming weaker and weaker as it runs away from the central body until at last the field is flat at infinity. It has yet to be seen whether and how this view of the distribution of energy is substantiated by the field equations of relativity.

Milne has called into question the logic of the relativistic procedure by which the same field questions are supposed to be valid for local gravitational situations and for the gravitational situation of the world as a whole. As we have already mentioned Einstein formulates in this manner Mach's idea that inertia as well as gravitation is conditioned by interaction. In the cosmological solution there is no boundary condition at infinity because infinity itself is abolished. But for the solutions of other gravitational problems we can no longer adopt the old boundary condition (D). At great distances from an isolated material system the cosmologi-

* See in this connection (17⁴) and (17⁵).

cal field will assert itself and as the space-time structure must be continuous a new boundary condition must replace (D). The cosmological phenomena favour a special space-time frame which has to be recognised as a physical reality by itself in contradistinction to the spirit of relativity. This frame of a cosmic space and a cosmic time will influence the field through the new boundary condition. In Einstein's new relativity the boundary condition is still taken as (D) because it ensures the uniqueness of a solution. Although we do not fully agree with Milne's criticism on the point we recognise that general relativity needs to be modified so as to give a logical presentation of local gravitational phenomena and the world structure.

In a dynamical problem we have to find the value of certain observables at any time, given their values at a particular instant. General relativity does not tell us how this can be achieved in an unambiguous manner in all cases. The root of the difficulty is the lack of precision in defining the common boundary of matter and field by sufficient mathematical conditions. So long as a purely field theory of gravitation has not been constructed and matter and field are to be recognised as two independent realities the objection on the score of ambiguity of boundary conditions remains a very important one.

9. CERTAIN APPLICATIONS OF GENERAL RELATIVITY

In a recent paper by Eddington and Clark* the surprising result is obtained that the total energy of a system of gravitating particles is

$$E = T + V + \frac{1}{2} \frac{d^2 C}{dt^2} \quad (9.1)$$

where T is the kinetic energy, V is the potential energy and C is the moment of inertia of the system about its centre of mass. The total energy of the system is, therefore, no longer constant. Their line-element for the field of n -particles is given by

$$\left. \begin{aligned} g_{11} = g_{22} = g_{33} = -1 + 2 \frac{\sum_i m_i}{\sum_{\mu} m_i} \frac{r_i}{(v_{\mu})_i} r_i, \quad g_{12} = g_{23} = g_{31} = 0 \end{aligned} \right\} \quad (9.2)$$

while

$$g_{44} = 1 + \gamma_0 + \frac{1}{2} \dot{\gamma}_0^2 + \sum_i \left(-\frac{3m_i v_i^2}{r_i} + \frac{2m_i}{r_i} \sum_j \frac{m_j}{\Delta_{ij}} - m_i \frac{\partial^2 r_i}{\partial t^2} \right) \quad (9.3)$$

where $\gamma_0 = -2 \sum_i m_i / r_i$,

in the usual notation. This line-element does not assume the

* *c. f.* (5f).

Galilean form at infinity because of the term $-\sum_i m_i \frac{\partial^2 r_i}{\partial t^2}$ in (9.3).

Now this term would be zero if the acceleration of the centre of mass vanishes. But there is no reason to suppose that this acceleration vanishes as the masses change their values with changing velocities. It may, however, be reasonable to suppose that this term is a small one. Eddington and Clark make no such assumption about the term but they ignore it while evaluating the total energy on grounds that it is the correction for retarded potentials. It may be recalled that the formula for a retarded potential is*

$$\frac{m}{[r(1-v_r)]} = \frac{m}{r} + \frac{1}{2}m \frac{\partial^2 r}{\partial t^2} + \dots \quad (9.4)$$

by Lagrange's expansion. If, therefore, the term $\sum_i m_i \frac{\partial^2 r_i}{\partial t^2}$ is ignored then, according to the general relativistic result, we ought to have a conserved energy. This certainly contradicts the result (9.1). The difficulty caused by the term $-\sum_i m_i \frac{\partial^2 r_i}{\partial t^2}$ deserves a careful consideration. If it is not negligible the field ceases to be Galilean at infinity and we have no criterion left by which to decide whether the present solution of the problem is right and unique. In his solution of the problem of n -bodies Einstein† and others write: "In the determination of the field and the equations of motion non-Galilean values at infinity and singularities of the type of dipoles, quadrupoles, and higher poles, must be excluded from the field in order that the solution shall be unique."

Incidentally it is interesting to find that, following quite a different procedure Einstein and others have found a line-element which agrees with the value of g_{44} in (9.3). All that‡ we need do is to consider the value given by these workers, in their own notation, of g_{44} by

$$g_{44} - 1 = \lambda^2 h_{24} + \lambda^4 h_{44} = \frac{1}{2} \gamma_{24} \lambda^2 + \frac{1}{2} \gamma_{44} \lambda^2 + \frac{1}{2} \gamma_{44} \lambda^4 + \frac{1}{2} \gamma_{44} \lambda^4 \quad (9.5)$$

The suffix '0' is used in place of '4' in the work quoted above. In this case, however, there is no difficulty arising out of the term $-\sum_i m_i \frac{\partial^2 r_i}{\partial t^2}$. The acceleration of the centre of mass is shown

* c f. (5a), p. 253.

† See (5f).

‡ Note the remarks on p. 87 following (11.62).

to be zero and so, in spite of the presence of the term, the line-element becomes Galilean at infinity. It is astonishing nevertheless that Eddington and Clark, having used a stress tensor $T_{\mu\gamma}$ arrive at the same form of g_{44} which Einstein and others get by following quite an independent method and making no use of $T_{\mu\gamma}$.

We believe that the comparison which has led to the result (9.1) is faulty. The line-element of any isolated system can be compared at great distances with the line-element given by Schwarzschild, *viz.*,

$$ds^2 = - \left(1 + \frac{M}{2r}\right)^4 (dx_1^2 + dx_2^2 + dx_3^2) + \frac{(1 - M/2r)^2}{(1 + M/2r)^2} dx_4^2 \quad (9.6)$$

or, writing $\gamma_M = -2M/r$, as Eddington and Clark do,

$$ds^2 = -(1 + \gamma_M + \dots)(dx_1^2 + dx_2^2 + dx_3^2) + (1 + \gamma_M + \frac{1}{2}\gamma_M^2 + \dots)dx_4^2 \quad (9.7)$$

If $h_{\mu\gamma}$ denote the departures from the Galilean field,

$$\gamma_{00} \equiv \gamma_{44} = \frac{1}{2}(h_{11} + h_{22} + h_{33} + h_{44}) = \gamma_M. \quad (9.8)$$

When we compare Einstein's solution with (9.7)

$$\gamma_M = \lambda^2 \gamma_{44} + \lambda^4 \gamma_{44} \quad (9.9)$$

and this gives the energy of the system as

$$E = T + V + \Sigma m, \quad (9.10)$$

The reason why the comparison made by Eddington and Clark is faulty is this. γ_M contains terms of the first as well as the second order of masses. Hence γ_M^2 also contains terms of the second order of masses. Some of the terms of their line-element which correspond to a part of γ_M^2 have therefore been wrongly taken up, being of the second order of masses, for comparison with γ_M . We shall now direct our attention to the general question of the calculation of energy which crops up in the classical treatment of the problem of n -bodies and in several other problems.

The energy of an isolated material system, surrounded by Galilean space-time is given by the formula,*

$$J_4 = \iiint (T_4^4 - T_1^1 - T_2^2 - T_3^3) \sqrt{-g} \, dx \, dy \, dz + \frac{1}{2} \pi \iiint g^{\alpha\beta} \sqrt{-g} \frac{\partial}{\partial t} \left[- \left| \alpha\beta \right|^4 + \frac{1}{2} g_{\alpha}^4 \left| \beta \right|^2 + \frac{1}{2} g_{\beta}^4 \left| \alpha \right|^2 \right] dx \, dy \, dz \quad (9.11)$$

If the field is a static one, the formula takes the simpler form

$$J_4 = \iiint (T_4^4 - T_1^1 - T_2^2 - T_3^3) \sqrt{-g} \, dx \, dy \, dz \quad (9.12)$$

* *c.f.* (31).

In the case of Schwarzschild's internal solution it can be easily verified that

$$J_4 = \iiint (\rho + 3p) \sqrt{-g} \, dr \, d\theta \, d\phi = \frac{4\pi\rho}{3} \int_0^{r_1} 3r^2 dr = m, \quad (9.13)$$

where r_1 is the radius of the sphere and m is the constant that appears in the external solution. The formula for energy may be written in this particular case in the form,

$$m = \int (\rho + 3p) \sqrt{-g_{11}g_{22}g_{33}g_{44}} \, d\tau \quad (9.14)$$

which is the same as

$$m = \int (\rho + 3p) \sqrt{-g_{11}g_{22}g_{33}} (1 + \frac{1}{2} \log g_{44}) \, d\tau, \quad (9.15)$$

to the second degree of approximation. As the boundary is defined by the condition $p=0$ at $r=r_1$,

$$\int 3p \sqrt{-g_{11}g_{22}g_{33}} \, d\tau + \frac{1}{2} \int \rho \log g_{44} \, d\tau = 0, \quad (9.16)$$

a result, which has been proved by Tolman. Hence

$$m = \int T \sqrt{-g_{11}g_{22}g_{33}} \, d\tau \quad (9.17)$$

where

$$T = \rho - 3p \quad (9.18)$$

To the second order of approximation the energy-density of the sphere is $\rho - 3p$.

It is sometimes remarked that mass for mass radiation is a more effective attracting agent than matter*. Tolman has also given an illustration where radiation is found to attract with twice the efficiency of matter.† We show in following that this strange result is due to a mistake in the usual method of assessing the energy of radiation. It is well-known that in a weak field of gravitation where the departure of $g_{\mu\nu}$ from the Galilean values is measured by $h_{\mu\nu}$, the force of the field is

$$-\frac{1}{2} \frac{\partial h_{44}}{\partial x}, \quad -\frac{1}{2} \frac{\partial h_{44}}{\partial y}, \quad -\frac{1}{2} \frac{\partial h_{44}}{\partial z} \quad (9.19)$$

In the notation of retarded potentials‡ the solution gives

$$h_{44} = -2 \int \frac{(T_4^4 - T_1^1 - T_2^2 - T_3^3)' \sqrt{-g'}}{r'} \, d\tau' \quad (9.20)$$

$$\text{For radiation} \quad T_1^1 + T_2^2 + T_3^3 + T_4^4 = 0 \quad (9.21)$$

$$\text{Hence} \quad h_{44} = -4 \int \frac{T_4^4 \sqrt{-g'}}{r'} \, dv' \quad (9.22)$$

For matter the components T_1^1, T_2^2, T_3^3 are small compared to T_4^4 and so the force of radiation as given by the potential in

* c.f. (5c), p. 51.

† c.f. (31), p. 278.

‡ c.f. (5a), p. 129.

(9.22) is found to be approximately double the force of matter as given by the potential in (9.20). But when we note that the energy-density of radiation is $2T_4^4$ while that of matter is approximately T_4^4 we understand why radiation appears to be twice as effective as an agent of attraction.

Of the phenomena of great astronomical interest the one with reference to which general relativity has not so far advanced a satisfactory explanation is the spiral structure of the extra-galactic nebulae. These are the largest and heaviest bodies known to us the average mass of a nebula being about 10^{10} suns and the average diameter about 10^4 light years. In an investigation of the world-structure the nebulae are usually treated as fundamental particles. Unlike most of the smaller bodies of the universe the nebulae are flat structures not spherical. This is in contradiction to Liapounoff's* theorem that a fluid mass left to itself in free space assembles in a spherical form as it is one of minimum energy. On a closer investigation the plane structures are found to be spirals, with several convolutions, but with numerous peculiarities and differences of internal details. Assuming that the spiral structure is due to a movement of particles in spirals an attempt was made to find out a space-time field and the corresponding distribution of matter permitting spirals as geodesics. For the sake of mathematical convenience a line-element was taken of the form†

$$ds^2 = -e^\mu (dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2) + e^\gamma dt^2 \quad (9.23)$$

with $\mu = \mu(r, t)$, $\gamma = \gamma(r, t)$;

and the energy-tensor was assumed to be

$$T_\mu^\gamma = (p + \rho)v_\mu v^\gamma - pg_\mu^\gamma \quad (9.24)$$

It can be shown that $v^2 = v^3 = 0$; and so the components T_μ^γ satisfy identically the condition,

$$e^\gamma [T_1^4]^2 = e^\mu (T_4^4 - T_2^2)(T_2^2 - T_1^2) \quad (9.25)$$

(9.25) is the condition of isotropy as the tensor T_μ^γ itself, as defined by (9.24) is isotropic. The condition of isotropy gives the differential equation

$$4e^{-\gamma} (\dot{\mu}\gamma')^2 - [2\gamma'' + \gamma'^2 - 2\gamma'/r] [4e^{-\gamma}\ddot{\mu} - e^{-\mu}(2\gamma'' + \gamma'^2 + 2\gamma'/r)] = 0, \quad (9.26)$$

where a dot denotes a differentiation with regard to time and a

* c.f. (1).

† c.f. (17e) and (17g).

dash with regard to r . It gives the solution

$$e^\gamma = r^2, \quad e^\mu = A + Bt + \frac{1}{2}t^2, \quad (9.27)$$

A and B being arbitrary constants of integration. The density is if $A = B = 0$,

$$T_4^4 = (3/r^2 - \lambda t^2)/8\pi t^2. \quad (9.28)$$

The radial equation, supplied by the geodesics, is

$$\ddot{r} - \dot{r} \left[\frac{(B+t)\dot{r}^2}{2r^2} + \frac{2\dot{r}}{r} \right] \frac{(B+t)\dot{r} + r}{A+Bt+\frac{1}{2}t^2} = 0 \quad (9.29)$$

This has a solution of the former,

$$\dot{r}/r = \lambda/t, \quad (9.30)$$

if A and B are assumed to be zero. Another integral provided by the equations of geodesics is

$$\phi = \sqrt{(2 - \lambda^2)}/t \quad (9.31)$$

Equations (9.30) and (9.31) give tracks which are equiangular spirals. It is also interesting to note that the radial motion is similar to that of Milne's fundamental particles. The main difficulty in connection with the nebulae, as we have remarked above, is to explain first why they are plane and afterwards the numerous details of internal structure.

The principle of conservation of energy is established in relativity only for finite isolated systems. For finite material systems which do not satisfy the postulate (D) the principle is not true. The definition of energy of a finite world-model is purely arbitrary and it has not behind it the sanction of the general theory. To say further that the energy so defined is conserved is nothing short of making a new hypothesis. Moreover, the energy of a world-model depends upon the convention that we adopt regarding the energy-density and also upon the space-time frame of the model. Consider, for instance, the model of a non-static universe given by

$$ds^2 = dt^2 - R^2(t) \frac{dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2}{\left(1 + \frac{kr^2}{4}\right)^2}, \quad k = \pm 1, 0 \quad (9.32)$$

The material content of the model is given by Einstein's equations. The first question that arises is as to what should be the density of energy, ρ , $\rho - 3p$ or $\rho + 3p$. All these expressions are scalar invariants,* ρ is the invariant $T_{\mu\gamma} v^\mu v^\gamma$, $\rho - 3p$ is the invariant $T_{\mu\gamma} \rho^{\mu\gamma}$, while $\rho + 3p$ features as the density of energy as shown

* c.f. (17k.)

in (9.14). We have no good reason to accept any one of the three as the energy-density and it would be more logical to evaluate the energy by the formula,

$$J_4 = \int_0^{2\pi} \int_0^\pi \int_0^l (T_4^4 \sqrt{-g} + f_4^4) dr d\theta d\phi \quad (9.33)$$

where for $k=1, 0$ the limit l is ∞ and for $k=-1$ it is 2 and

$$f_4^4 = \frac{1}{16\pi} \left[-\frac{\delta}{\delta x^4} (g_{\mu r} \sqrt{-g}) \left\{ -\left[\mu r + \frac{1}{2} g_{\mu}^4 \right] r s + \frac{1}{2} g_r^4 \left[\mu s \right] \right\} \right. \\ \left. - g_4^4 g^{\mu r} \sqrt{-g} \left\{ -\left[\mu \alpha \right] r \beta + \left[\mu r \right] \alpha \beta \right\} + 2 g_\beta^\alpha \lambda \sqrt{-g} \right] \quad (9.34)$$

For the line-element (9.32)

$$8\pi (T_4^4 \sqrt{-g} + f_4^4) = \frac{R \sin \theta}{\left(1 + \frac{kr^2}{4}\right)^2} \left[-1 + \frac{7}{2} kr^2 - \frac{1}{16} k^2 r^4 \right] \quad (9.35)$$

For $k=+1$, that is, for a finite and spherical universe,

$$J_4 = \frac{\pi}{4} R \quad (9.36)$$

For $k=-1$ or 0 the value of J_4 is, surprisingly enough, $-\infty$. Thus the total energy for a hyperbolic universe such as the one considered by Milne or McVittie turns out to be negative and infinite while J_4 is positive and finite only for a closed or spherical universe. In an expanding spherical universe the energy increases with radius. There is no reason to suppose that J_4 so calculated is the correct estimate of energy. Our contention is that the concept of energy itself as used in the discussion of a world-model is something quite different from the concept of energy which finds expression in the treatment of finite isolated systems. All the difference is caused by the absence of the postulate (D) in the mathematics that takes control of the problem. But if it is permissible to use Einstein's equations for the study of the world-model and if the concept of energy is to play a part in the mathematical representation the evaluation of the latter ought to be done by the method sketched above. This is the only method that gives the combined energy of field and matter.

10. SULAIMAN'S CRITICISMS*

We have no intention to give here an account of Sir Shah Sulaiman's theory of gravitation. His investigations have taken

* c.f. (26a) and (26b).

many turns and the theory has assumed a novel shape at each stage of investigation. Sulaiman started by telling us that the key to gravitation is in the gravitons; now we understand that the genesis of gravitation is in a slight excess of electric attraction over repulsion. But we have not understood his logic, not even the reason why he calls his theory "A New Relativity". So we will be concerned here with what are understood to be his chief criticisms of general relativity.

There are only two alternative interpretations possible of the *Michelson-Morley experiment*. One is that the velocity of light is absolute and independent of the source while the other is that the earth is at absolute rest in aether. The earth moves relative to the sun with an average velocity of 30 km. per second. The sun moves relative to the Central Galaxy with an average velocity of 300 km. per second. About the motion of the Central Galaxy itself we know very little. Our knowledge of the world-structure is not sufficiently advanced for the purpose. If the earth is at rest the sun has an absolute motion about it and so also the Central Galaxy. By its physical characteristics the earth is not in any way more qualified than any other planet or star to occupy the distinguishing position of absolute rest. The hypothesis of the earth at rest in aether gives man a central position in the universe which is not warranted by physical facts. The scientists have therefore regarded the hypothesis as unpalatable. Whether Sulaiman agrees with this or not he cannot persuade himself that the light-hypothesis is more palatable. If we look upon light as a wave motion in an all-pervading aether (by which we do not mean an absolute space-time frame) the velocity of light is an absolute constant of the medium. This makes the light-hypothesis perfectly palatable. Moreover, as de Sitter has shown, if the light-hypothesis is not adopted the established agreement between theory and observation regarding the double stars is thoroughly unsettled.

If the corpuscular view of light is adopted the light corpuscles obey a new kinematics according to the hypothesis. It is argued by Sulaiman that aberration can be explained strictly according to classical kinematics. But it may be pointed out that even special relativity, based on the light-hypothesis, can explain aberration*. At any rate it is no proof that relativity is wrong if the classical theory explains aberration.

Sulaiman considers that the law of repulsion which results from the cosmical term is absurd. The law does not contradict

* c.f. (136).

the theory; does not contradict observation; does not contradict commonsense because the law governs phenomena which are far beyond common experience. As far as I can see Sulaiman considers the law absurd because it conflicts with his private intuition. Now and then science does introduce to us a new idea which our intuition is not prepared to welcome. When the idea is proved successful and assimilated well in our habits of scientific thought private intuition ceases to be hostile to it.

It must be clearly understood that the superiority of general relativity over Newton's theory does not lie merely in satisfying the three crucial tests. As an empirical theory Newton's is so successful that it can be modified mathematically in any number of ways so as to satisfy the three tests. One such modification is presented by Sulaiman himself. All such modifications are open to the criticism to which Newton's ideology is subject and as they replace the beautifully simple Newtonian law they aggravate the formal difficulties of the theory. The scientist is not only interested in the right answer but in the right method as well. Sulaiman appears to have concentrated so far in getting only the right answer.

General relativity accounts for the motion of the perihelion of Mercury. As regards the deflection of light the recent work of Freundlich led to the impression that even Einstein's theory does not account for the full effect. As an excess value may arise as an atmospherical effect Dyson and Woolley* consider that general relativity has satisfied even this crucial test. About the third test, concerning the spectral shift of the sun, there is some doubt caused by the 'edge-effect', certain rays from the edge showing twice the relativistic effect. The light from the centre confirms general relativity and experts are inclined to look for an explanation of the edge-effect outside general relativity.

May be that a decisive observational test of the future fails to confirm general relativity. We have already shown numerous defects of the theory. A more accurate theory may displace general relativity. A conscientious student of the subject cannot deny the great virtue of Einstein's representation of gravitation embodied in the principle of relativity and the clarification of our fundamental ideas of space, time and matter resulting therefrom. The principle of relativity must be looked upon as a principle of uniformity of nature and, to be able to explain matter and motion as a uniformity of nature, is an achievement of supreme art and scientific genius.

* c.f. (4).

III

11. THE SOLUTION OF THE n -BODY PROBLEM
BY EINSTEIN AND OTHERS.

The problem that the authors have tried to solve in this paper is the celebrated n -body problem.* Each body is treated as a structureless particle so that the complication of the gravitational effect on shapes of bodies does not set in. As the treatment requires a clear-cut separation between space and time right from the beginning the '0' suffix is used to denote the time co-ordinate. According to the convention adopted Latin indices take on only the spatial values 1, 2, 3, while Greek indices refer to both space and time and run over 0, 1, 2, 3.

The flat Galilean space is indicated by the matrices, $\eta^{\mu\gamma}$ and $\eta_{\mu\gamma}$ whose principal diagonals alone have non-zero members, being +1, -1, -1, -1, in order. An auxiliary time-co-ordinate τ is used so that

$$\tau = \lambda x^0, \quad (11.1)$$

and if ϕ is any function of space-and-time variables, $\partial\phi/\partial\tau$ is of the same order as $\partial\phi/\partial x^m$. In natural co-ordinates the velocity of light c is expressed by unity and so the time-derivative is usually small compared to a space-derivative. As

$$\frac{\partial\phi}{\partial x^0} = \lambda \frac{\partial\phi}{\partial\tau}, \quad (11.2)$$

λ is a small parameter. Its order is defined by the ratio of the average velocity of a particle to that of light. The fundamental tensor $g_{\mu\gamma}$ is expressed in the form

$$g_{\mu\gamma} = \eta_{\mu\gamma} + h_{\mu\gamma} \quad (11.3)$$

to bring out clearly the gravitational effects represented by $h_{\mu\gamma}$. It is assumed that $h_{\mu\gamma}$ can be expanded in a power series in λ . There are certain linear combinations of $h_{\mu\gamma}$ which occur frequently in the calculations and in order to facilitate the work we will denote them by $\gamma_{\mu\gamma}$:

$$\gamma_{\mu\gamma} = h_{\mu\gamma} - \frac{1}{2} \eta_{\mu\gamma} \eta^{\sigma\rho} h_{\sigma\rho}, \quad (11.4)$$

or, more explicitly,

$$\gamma_{00} = \frac{1}{2} h_{00} + \frac{1}{2} h_{ii} \quad (11.5)$$

$$\gamma_{0n} = h_{0n}$$

$$\gamma_{mn} = h_{mn} - \frac{1}{2} \delta_{mn} h_{ii} + \frac{1}{2} \delta_{mn} h_{00}$$

δ_{mn} are the usual kronecker deltas and they need no definition

* c.f. (24a) and (5j).

here. The usual equations of a weak gravitational field with a distribution of matter $T_{\mu\gamma}$ are given by

$$\gamma_{\mu\gamma,\sigma\sigma} = -2T_{\mu\gamma}, \quad (11.6)$$

where a suffix after a comma will be supposed to stand for the corresponding differentiation; by a suffix '0' coming after a comma we will mean a differentiation with respect to τ . Now

$$T_{\mu\gamma} = \rho \frac{d\xi^\mu}{ds} \frac{d\xi^\gamma}{ds} \quad (11.7)$$

and hence we will take γ_{00} to be of the order of λ^2 , γ_{0n} of the order of λ^3 and γ_{mn} of the order of λ^4 . Although, in the problem under consideration, the tensor $T_{\mu\gamma}$ is not incorporated we will assume that the orders of magnitude of the different γ 's are as in this particular case. We will further assume

$$\gamma_{00} = \lambda^2 \gamma_{00}^{(2)} + \lambda^4 \gamma_{00}^{(4)} + \lambda^6 \gamma_{00}^{(6)} + \dots \quad (11.8)$$

$$\gamma_{0n} = \lambda^3 \gamma_{0n}^{(3)} + \lambda^5 \gamma_{0n}^{(5)} + \lambda^7 \gamma_{0n}^{(7)} + \dots$$

$$\gamma_{mn} = \lambda^4 \gamma_{mn}^{(4)} + \lambda^6 \gamma_{mn}^{(6)} + \lambda^8 \gamma_{mn}^{(8)} + \dots$$

The coefficients of the different powers of λ are self-explanatory. The omitted powers of λ in the above expansion stand for a retarded potential. It is found that their inclusion does not affect the equations of motion. In view of (11.2) and (11.8) we find that the expansions for Christoffel symbols, for $h_{\mu\gamma}$ and their derivatives and for $G_{\mu\gamma}$ conform to the following rule:

"Any component having an odd number of zero suffixes will have only odd powers of λ in its expansion, while any component having an even number of such suffixes will involve only even powers of λ in its expansion." [6e, p.75].

With this rule in view we now write the explicit form of the equations $G_{\mu\gamma} = 0$ as follows:—

$$G_{00} \equiv -\frac{1}{2} h_{00,ss} + L_{00} = 0 \quad (11.9)$$

$$G_{0n} \equiv -\frac{1}{2} h_{0n,ss} + \frac{1}{2} \gamma_{ns10s} + \frac{1}{2} (\gamma_{os1s} - \gamma_{oo1o})_{1n} + L_{0n} = 0$$

$$G_{mn} \equiv -\frac{1}{2} h_{mn,ss} + \frac{1}{2} \gamma_{ms1sn} + \frac{1}{2} \gamma_{ns1sm} + L_{mn} = 0$$

Here the bar '1' serves the same purpose as the comma except for the suffix '0' which follows and which means now a differentiation with respect to x^0 . Thus ϕ_{1s} and $\phi_{,s}$ is the same but ϕ_{10} means $\partial\phi/\partial x^0$ while $\phi_{,0}$ means $\partial\phi/\partial\tau$. The residual terms are denoted by $L_{\mu\gamma}$ in the above. We will now give the reason of splitting up and grouping the terms of $G_{\mu\gamma}$ as in the above. First of all four restrictions can be put on the co-ordinate systems. They are

$$\gamma_{0s1s} - \gamma_{0010} = 0. \quad (11.10)$$

$$\gamma_{mn1s} = 0$$

These equations simplify the form of (11.9) which now become

$$\begin{aligned} h_{00, ss} &= 2 L_{00} \\ h_{0n, ss} &= 2 L_{0n} \\ h_{mn, ss} &= 2 L_{mn} \end{aligned} \quad (11.11)$$

Note the expressions for $L_{\mu\gamma}$ which are given below :—

$$\begin{aligned} L_{00} &= h_{0s} 1_{0s} - \frac{1}{2} h_{ss} 1_{00} - (h^{\sigma\lambda} \bar{\lambda}_{00, \sigma}) 1_{\lambda} \\ &\quad + \left(h^{\lambda\sigma} \bar{\lambda}_{0\lambda, \sigma} \right)_{10} + \bar{\lambda}_{\sigma}^{\lambda} \bar{\lambda}^{\sigma} - \bar{\lambda}^{\lambda} \bar{\lambda}_{\sigma}^{\sigma} \\ L_{0n} &= - \left(h^{\lambda\sigma} \bar{\lambda}_{0n, \sigma} \right)_{1\lambda} + \left(h^{\lambda\sigma} \bar{\lambda}_{n\lambda, \sigma} \right)_{10} \\ &\quad + \bar{\lambda}_{n\sigma}^{\lambda} \bar{\lambda}_{\lambda 0}^{\sigma} - \bar{\lambda}_{n0}^{\lambda} \bar{\lambda}_{\lambda\sigma}^{\sigma} \\ L_{mn} &= - \frac{1}{2} h_{0m} 1_{0n} - \frac{1}{2} h_{0n} 1_{0m} + \frac{1}{2} h_{mn} 1_{00} \\ &\quad - \left(h^{\lambda\sigma} \bar{\lambda}_{mn, \sigma} \right)_{1\lambda} - \left(h^{\lambda\sigma} \bar{\lambda}_{m\lambda, \sigma} \right)_{1n} \\ &\quad + \bar{\lambda}_{m\sigma}^{\lambda} \bar{\lambda}_{n\lambda}^{\sigma} - \bar{\lambda}_{mn}^{\lambda} \bar{\lambda}_{\lambda\sigma}^{\sigma} \end{aligned} \quad (11.12)$$

The order of L_{00} is λ^4 , that of L_{0n} is λ^5 while that of L_{mn} is λ^4 . What is significant is that all the 'h'-terms which are involved linearly in $L_{\mu\gamma}$ are time-derivatives. This permits the solution to be worked out by successive approximations. Before we proceed to do this we will cast the equations (11.11) into another form involving $\gamma_{\mu\gamma}$ as the co-ordinate conditions are couched in terms of γ 's. Thus

$$\begin{aligned} \gamma_{00, ss} &= 2 \Lambda_{00}, \\ \gamma_{0n, ss} &= 2 \Lambda_{0n}, \\ \gamma_{mn, ss} &= 2 \Lambda_{mn}, \end{aligned} \quad (11.13)$$

where the formulae of connection between $L_{\mu\gamma}$ and $\Lambda_{\mu\gamma}$ are exactly like formulae connecting $h_{\mu\gamma}$ with $\gamma_{\mu\gamma}$, viz., (11.5). We have

$$\begin{aligned} \Lambda_{00} &= \frac{1}{2} L_{00} + \frac{1}{2} L_{00} \\ \Lambda_{0n} &= L_{0n} \\ \Lambda_{mn} &= L_{mn} - \frac{1}{2} \delta_{mn} L_{00} + \frac{1}{2} \delta_{mn} L_{00} \end{aligned} \quad (11.14)$$

To bring out the significance of differentiation with respect to γ we will adopt the convention of suffixes under '0' as illustrated in the following :—

$$h_{mn} 1_{0s} = \lambda h_{mn}, 0s = \lambda^5 h_{mn}, 0s + \lambda^5 h_{mn}, 0s + \lambda^7 h_{mn}, 0s + \dots (11.15)$$

The gravitational equations (11.13) now expand into

$$\sum_{l=1}^{\infty} \lambda^{2l} \left(\gamma_{oo, ss-2} \frac{\Delta_{oo}}{2l} \right) = 0, \quad (11.16)$$

$$\sum_{l=1}^{\infty} \lambda^{2l+1} \left(\gamma_{on, ss-2} \frac{\Delta_{on}}{2l+1} \right) = 0, \quad (11.17)$$

$$\sum_{l=1}^{\infty} \lambda^{2l} \left(\gamma_{mn, ss-2} \frac{\Delta_{mn}}{2l} \right) = 0, \quad (11.18)$$

while the co-ordinate conditions become

$$\sum_{l=1}^{\infty} \lambda^{2l+1} \left(\gamma_{oo, o-1} \frac{\Delta_{on}}{2l+1} \right) = 0 \quad (11.19)$$

$$\sum_{l=1}^{\infty} \lambda^{2l} \gamma_{nm, n} = 0 \quad (11.20)$$

For $l=1$ we get ten independent equations which we solve and obtain h_{oo}, h_{on}, h_{mn} . It is found that $\Delta_{\mu\gamma}$ vanish for $l=1$. For $l=2$ we substitute the values of h 's in $\Delta_{\mu\gamma}$ and we get equation to determine h_{oo}, h_{on}, h_{mn} . We can further make use of these values in $\Delta_{\mu\gamma}$ for $l=3$ and thus obtain equations to determine h_{oo}, h_{on}, h_{mn} . At each stage the equations that we have to solve are of the form

$$\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2} = P(xyzt) \quad (11.21)$$

where P is a known function. Another type of equations is presented by the co-ordinate conditions at each stage. The line-element can be determined in this manner, with a number of arbitrary functions entering in at each stage. But our interest is in a definite line-element for the n -body problem and we will now turn to the dynamical question of motion.

Suppose that we temporarily relax the co-ordinate conditions and replace them by

$$\gamma_{oo, 10} - \gamma_{on, 1n} = - \sum_{k=1}^P \left\{ \frac{k}{C_o/r} \right\} \quad (11.22)$$

$$\gamma_{nm, 1n} = - \sum_{k=1}^P \left\{ \frac{k}{C_m/r} \right\} \quad (11.23)$$

where $\frac{k}{r}$ is the distance from x^n to the k-singularity :

$$\frac{k}{r} = \left[(x^1 - \xi^1)(x^2 - \xi^2) \right]^{1/2} \quad (11.24)$$

$\frac{k}{C_0}$ and $\frac{k}{C_m}$ are certain function of τ defined at the k-singularity by the integrals,

$$\frac{1}{4\pi} \int \frac{k}{r} (\gamma_{00} l_{0n} - 2\Delta_{0n}) \cos(n \cdot N) ds = \frac{k}{C_0}(\tau) \quad (11.25)$$

$$\frac{1}{4\pi} \int \frac{k}{r} \Delta_{mn} \cos(M \cdot N) ds = \frac{k}{C_m}(\tau) \quad (11.26)$$

The surfaces are arbitrary as in Stokes' theorem and they enclose only the k-singularity. N indicates the direction of the outward normal to the surface at a point. It is possible to choose such an arbitrary surface for (11.25) only if

$$(\gamma_{00} l_{0n} - 2\Delta_{0n}) l_n = 0, \quad (11.27)$$

holds good everywhere except at the singularity. Using (11.13) we find that (11.27) reduces to

$$(\gamma_{00} l_0 - \gamma_{0n} l_n) l_{ss} = 0 \quad (11.28)$$

which is certainly true in view of (11.22). Similarly we can justify the choice of an arbitrary surface for the integral (11.26). If the field-equations hold good everywhere and if they are made to break down for the sake of analytic continuation in conformity with (11.22) and (11.23) within a neighbourhood of each singularity the above representation is justifiable. As Einstein and others put it, "Such a continuation is possible for any surfaces surrounding the singularities and can be made in such a way that when these surfaces shrink to zero size the function $\Delta_{mn} l_n$ ($\Delta_n l_n$ in Einstein's notation) goes over to a sum of Dirac δ -functions :

$$\Delta_{n1n} \rightarrow 4\pi \sum_{K=1}^K C(\tau) \delta(x^1 - \xi^1) \delta(x^2 - \xi^2) \delta(x^3 - \xi^3). \quad (11.29)$$

Outside the surfaces enclosing the singularities the following equations hold good :—

$$\left. \begin{aligned} \Delta_{0010} - \Delta_{0n1n} &= 0 \\ \Delta_{mn1n} &= 0 \end{aligned} \right\} \quad (11.30)$$

These equations take the roll of co-ordinate conditions. From these conditions and from the field-equations we can easily prove, by the use of analytic continuation and the Gauss theorem, that the equations (11.22) and (11.23) follow.

It will be understood that if $\frac{k}{C}=0$ the original co-ordinate μ

conditions will hold good. As the time enters C through ξ^k and its derivatives these equations are not just identities. In fact the dynamical equations of motion for the k -particle are

$$\underset{\mu}{C} = 0 \quad (11.31)$$

In accordance with our scheme of successive approximations,

$$\sum \lambda^{2l+1} \frac{1}{4\pi} \int^k \left(\gamma_{00,0n} - 2 \underset{2l+1}{\Lambda}_{on} \right) \cos(n, N) ds \equiv \sum_{2l+1}^k C_0 \lambda^{2l+1} = 0 \quad (11.32)$$

$$\sum \lambda^{2l} \frac{1}{4\pi} \int^k 2 \underset{2l}{\Lambda}_{mn} \cos(n, N) ds \equiv \sum_{2l}^k C_m \lambda^{2l} = 0 \quad (11.33)$$

Actually only the three equations (11.33) supply all the information, the zero-equation (11.32) being responsible for no restriction on the motion of the singularities. The equation (11.32) is used as a normalization condition at each stage so that the solution does not lose its uniqueness. We will show later that an effect of this normalization is to rule out the motion of non-static masses. Another condition that must always be borne in mind, as the solution advances, is that the field must remain Galilean at infinity, being at the same time free of all other singularities. The normalization referred to above is carried out in the following manner:—

Consider the field equations,

$$\gamma_{00,ss} = 2 \underset{2l}{\Lambda}_{00} \quad (11.34)$$

$$\gamma_{on,ss} = \underset{2l+1}{\Lambda}_{on} \quad (11.35)$$

and the co-ordinate condition,

$$\gamma_{00,0} - \gamma_{on,n} = - \sum_{k=1}^k \left\{ C_0(\tau) / r^k \right\} \quad (11.36)$$

if γ_{00} and γ_{on} are solutions of (11.34) and (11.35) so are also

$$\gamma'_{00} = \gamma_{00} + \sum_{k=1}^p \left\{ \frac{r^k}{r^k} \right\}, \quad (11.37)$$

$$\gamma_{on} = \gamma_{on} - \sum_{k=1}^p \left\{ \frac{r^k}{r^k} \right\} \quad (11.38)$$

and if

$$\left[\begin{matrix} k \\ 2l+1 \end{matrix} \right]_0 = \left[\begin{matrix} k \\ 2l+1 \end{matrix} \right]_0, \quad (11.39)$$

$$\begin{aligned} \gamma'_{oo,0} - \gamma'_{on,n} = \sum_{k=1}^p \left[\left\{ \left[\begin{matrix} k \\ 2l \end{matrix} \right] / \left[\begin{matrix} k \\ r \end{matrix} \right] \right\}_{\frac{0}{1}} + \left\{ \left[\begin{matrix} k \\ 2l \end{matrix} \right] \frac{k}{1} / \left[\begin{matrix} k \\ r \end{matrix} \right] \right\}_{,n} \right] \\ + \gamma_{oo,0} - \gamma_{on,n} \\ = 0, \end{aligned} \quad (11.40)$$

by virtue of (11.36) and (11.39). It is clear, therefore, that the condition (11.32) puts a restriction upon the solutions of (11.34) and (11.35). The motion itself is given by (11.33). The calculation of motion by stages of approximation will now be looked into.

The approximation $l=1$. A glance at the expressions for Δ_{oo} , Δ_{on} and Δ_{nn} shows that they are all zero. Hence $C_m = 0$ also and the equations of the field (11.13) and the co-ordinate conditions reduce to

$$\left. \begin{aligned} \gamma_{oo,ss} &= 0 \\ \gamma_{on,ss} &= 0 \\ \gamma_{oo,0} - \gamma_{on,n} &= 0 \end{aligned} \right\} \quad (11.41)$$

We will assume that the particles we are interested in have spherical symmetry and the field is Galilean at infinity. We will work out the case of two particles only and leave the case of n particles as no new principle is involved in the latter, more complicated, situation. Solving (11.41) we take

$$\gamma_{oo} = 2\phi, \phi = \psi + x, \psi = -2m/r, \chi = -2m/r^2, \dots (11.42)$$

$$\text{where } \left. \begin{aligned} (r)^{\frac{1}{2}} &= (x-\eta)^{\frac{1}{2}} + (x-\eta)^{\frac{2}{2}} + (x-\eta)^{\frac{3}{2}} \\ \text{and } (r)^{\frac{1}{2}} &= (x-\frac{1}{2})^{\frac{1}{2}} + (x-\frac{1}{2})^{\frac{2}{2}} + (x-\frac{1}{2})^{\frac{3}{2}} \end{aligned} \right\} \quad (11.43)$$

$$\text{As } \gamma_{on,n} = \gamma_{oo,0} = 2\dot{\phi} \text{ and } 2\Delta_{on} = 0, \quad (11.44)$$

$$\begin{aligned} \text{We find } \frac{1}{4\pi} \int_0^k (\gamma_{oo,0} - \gamma_{on,n} - 2\Delta_{on}) \cos(n \cdot N) ds &= C_0^k(r) \\ &= 4m = 0 \end{aligned} \quad (11.45)$$

Hence the masses are necessarily constant. There is no proof that the masses must be necessarily positive. Our justification,

in fact, for calling m^1 and m^2 masses is that they behave in the second approximation as Newtonian masses. From (11.44) we have

$$\gamma_{on} = -2\psi\eta^n - 2\chi\{^n \quad (11.46)$$

The line-element at this approximation is given by

$$h_{oo} = \psi + \chi, \quad h_{on} = -2\psi\eta^n - 2\chi\{^n, \quad h_{mn} = g_{mn}(\psi + \chi) \quad (11.47)$$

Owing to the vanishing of C_m^k there is no restriction on the motion at this stage. We write down for the calculation at the next

$$h_{oo}^{oo} = -h_{oo}, \quad h_{on}^{on} = h_{on}, \quad h_{mn}^{mn} = -h_{mn}. \quad (11.48)$$

The approximation $l=2$. The equation of the field (11.13) now becomes

$$\left. \begin{aligned} \gamma_{oo, ss} &= 2\Delta_{oo} = -\frac{2}{3}\phi, \quad s\phi, \quad s, \\ \gamma_{on, ss} &= 2\Delta_{on} = \phi, \quad s \quad \gamma_{os, n} - \phi, \quad sn \gamma_{os} - 3\phi, \quad o\phi, \quad n \\ \gamma_{mn, ss} &= 2\Delta_{mn} = -\gamma_{on, on} - \gamma_{on, on} + 2g_{mn}\phi, \quad oo \\ &\quad - 2\phi\phi, \quad mn - \phi, \quad m\phi, \quad n + \frac{2}{3}g_{mn}\phi, \quad s\phi, \quad s, \end{aligned} \right\} \quad (11.49)$$

while the co-ordinate conditions are

$$\left. \begin{aligned} \gamma_{oo, s} - \gamma_{on, n} &= 0 \\ \gamma_{mn, n} &= -(\dot{C}_m/\dot{r}) - (\dot{C}_m/\dot{r}) \end{aligned} \right\} \quad (11.50)$$

The equations of motion of the first particle are given by

$$\int_1^1 2\Delta_{mn} \cos(n-N) ds \equiv \dot{C}_m(\tau) = 0 \dots \quad (11.51)$$

Each term in the expression for Δ_{mn} is not solenoidal although the expression as a whole is. Hence while evaluating the integral (11.51), for the different terms of the integrand the same external surface must be chosen. We take the surface to be a sphere with a small radius the centre being at the singularity in question. Some of the integrals may become infinite but as the total must be finite the former ought to cancel out. In our evaluation of $\dot{C}_m(\tau)$ we shall therefore consider only those terms in the integrand which are likely to lead to a finite result. Those terms of the integrand which are of the order of $(1/r)^2$ are likely to make a non-zero and finite contribution.

The first term in $2\Delta_{mn}$ is $-\gamma_{om}$, on which may be fully written out as

$$-2\psi_{,ns} \dot{\eta}^m \dot{\eta}^s + 2\psi_{,n} \ddot{\eta}^m - 2\chi_{,ns} \dot{\eta}^m \dot{\eta}^s + 2\chi_{,n} \ddot{\eta}^m. \quad (11.52)$$

The only term that we need consider is the second as no other term is of the required order.

$$\frac{1}{4\pi} \int^1 2\psi_{,n} \ddot{\eta}^m \cos(n \cdot N) ds = 4m\ddot{\eta}^m \quad (11.53)$$

Similarly we get the contribution $\frac{4}{3}m\ddot{\eta}^m$ from $-\gamma_{on,om}$. The term $2\delta_{mn}\phi_{,oo}$ leads to

$$\begin{aligned} & -\frac{1}{4\pi} \int^1 2\delta_{mn} \frac{2m}{(r)^2} \dot{\eta}^l \cos(n \cdot N) ds \cdot \frac{x^l - \eta^l}{r} \\ & = -\frac{1}{4\pi} \int^1 \frac{4m\dot{\eta}^l}{(r)^4} (x^n - \eta^n)(x^l - \eta^l) \delta_{mn} ds = -\frac{4m}{3} \ddot{\eta}^m \end{aligned} \quad (11.54)$$

A new point arises in the evaluation of the fourth term, $-2\phi\phi_{,mn}$. A contribution can come only from the part $-2\psi_{,mn}\chi$ and in order to evaluate it χ must be expanded as a power series in the neighbourhood of the first singularity:—

$$\chi = \bar{\chi} + (x^s - \eta^s) \chi_{,s} + \quad (11.55)$$

The only term in the integrand which can give a finite result is $-2\psi_{,mn}(x^s - \eta^s) \bar{\chi}_{,s}$. The corresponding integral is

$$\begin{aligned} & \frac{1}{4\pi} \int (x^s - \eta^s) \psi_{,mn} \bar{\chi}_{,s} \cos(n \cdot N) ds \\ & = -\frac{4m\bar{\chi}_s}{4\pi} \int (x^s - \eta^s) (x^m - \eta^m) / \left(\frac{1}{r}\right)^4 \cdot ds \\ & = -\frac{4m}{3} \delta_{ms} \bar{\chi}_{,s} = -\frac{4m}{3} \bar{\chi}_{,m} \end{aligned} \quad (11.56)$$

Similarly the contributions from $-\phi_{,m}\phi_{,n}$ and $\frac{2}{3}\delta_{mn}\phi_{,ss}$ are $-\frac{8m}{3}\bar{\chi}_{,m}$ and $2m\bar{\chi}_{,m}$ respectively. Hence, combining all these

contributions, we get,

$$\frac{1}{4}C_m(\tau) \equiv \frac{1}{4\pi} \int^1 2\Delta_{mn} \cos(n \cdot N) ds - 4m(\ddot{\eta}^m + \frac{1}{2}\bar{\chi}_{,m}) = 0 \quad (11.57)$$

More explicitly, the equations of motion of the first particle are

$$m\ddot{\eta} = \text{grad} \left(\frac{1}{mm/r} \right), \quad (11.58)$$

r being the 'distance' between the two particles. The Newtonian

equations are thus obtained in the second approximation. It follows that the acceleration of the centre of mass is zero up to this order of approximation.

In the line-element the important term is γ_{00} , as it gives the expression of energy. From (11.49) we have

$$\gamma_{00} = -\frac{3}{4}\phi\phi + A\psi + B\chi, \quad (11.59)$$

where A and B are constants of integration. It will be noted that in this solution no fresh singularity is introduced. The constants A and B are to be determined by the conditions of normalization, viz.,

$$\frac{1}{4\pi} \int \left\{ \gamma_{00} - \gamma_{11} - 2\Lambda_{01} \right\} \cos(n \cdot N) ds = 0 \quad (11.60)$$

Evaluating the integral about the first singularity and using the equations of motion we derive

$$A = (\eta^s \eta^s + \frac{1}{2} \bar{\chi}) \quad (11.61)$$

Similarly, by integrating about the second singularity, we get

$$B = (\dot{\chi}^s \dot{\chi}^s + \frac{1}{2} \bar{\psi}) \quad (11.62)$$

We have already pointed out earlier that the total energy of the system is to be derived by comparing $\lambda^2 \gamma_{00} + \lambda^4 \gamma_{00}$ with the expression $-\frac{2M}{r}$ at large distances from the singularities.

Absorbing λ^2 in the masses and in the time-derivatives the total energy is found to be the familiar expression $(T + V + m^1 + m^2)$.

The derivation of the line-element is fraught with many difficulties. We will state here only the results.

$$\gamma_{mn} = \left\{ \psi [(x^n - \eta^n) \eta^m + (x^m - \eta^m) \eta^n - \delta_{mn} (x^s - \eta^s) \eta^s] \right\}_{,0} \quad (11.63)$$

$$+ \left\{ x [(x^n - \eta^n) \dot{\chi}^m + (x^m - \eta^m) \dot{\chi}^n - \delta_{mn} (x^s - \eta^s) \dot{\chi}^s] \right\}_{,0}$$

$$+ \frac{1}{4} (r)^2 \psi_{,m} \psi_{,n} + \frac{1}{4} (r)^2 \chi_{,m} \chi_{,n} - \psi_{,mn} (x^n - \eta^n) \bar{\chi} \\ + \psi [2\eta^m \eta^n + \delta_{mn} \bar{\chi}]$$

$$\gamma_{0m} = -\frac{1}{4} (r)^2 \psi_{,m} \psi_{,s} \eta^s + \frac{1}{4} \psi \psi_{,m} \eta^m - \frac{1}{2} (x^s - \eta^s) \psi \bar{\chi}_{,m} \dot{\chi}^s \\ - (x^m - \eta^m) \psi \bar{\chi}_{,s} \eta^s + \frac{1}{2} \psi_{,m} (x^s - \eta^s) \\ (x^1 - \eta^1) \bar{\chi}_{,s} \dot{\chi}^s + (x^m - \eta^m) \psi \bar{\chi}_{,s} \dot{\chi}^s.$$

$$+ \frac{1}{2} (x^s - \eta^s) \psi \bar{\chi}_{,s} \dot{\chi}^m + \frac{1}{2} (x^s - \eta^s) \psi \bar{\chi}_{,m} \eta^s + (x^s - \eta^s) \psi_{,m} \bar{\chi} \dot{\chi}^s$$

$$+ \psi [-\eta^s \eta^s \eta^m + \chi \eta^m - \bar{\chi} \dot{\chi}^m] \quad (11.64)$$

$$\gamma_{rr} = -2m^1 r_{,00} - 2m^2 r_{,00} + \frac{1}{2}\phi\phi + \psi(2\eta^s \eta^s + \frac{2}{3}\chi) + \chi(2\dot{\eta}^s \dot{\eta}^s + \frac{2}{3}\bar{\psi}) \quad (11.65)$$

The equations (11.59), (11.63) and (11.64) are enough to know the line-element.

The approximation $l=3$. At this stage we are not interested in the line-element at all. The evaluation of Δ_{mn} is sufficient for the solution of the dynamical problem. We find

$$\begin{aligned} C_m^1 &= \frac{1}{4\pi} \int^1 2\Delta_{mn} \cos(n-N) dS \quad (11.66) \\ &= -4m^1 m^2 \left\{ \left[\eta^s \eta^s + \frac{2}{3} \dot{\eta}^s \dot{\eta}^s - 4\eta^s \dot{\eta}^s - \frac{4m}{r} - \frac{5m}{r} \right] \frac{\delta}{\delta \eta^m} \left(\frac{1}{r} \right) \right. \\ &\quad \left. + [4\eta^s (\dot{\eta}^m - \eta^m) + 3\eta^m \dot{\eta}^s - 4\dot{\eta}^s \dot{\eta}^m] \frac{\delta}{\delta \eta^s} \left(\frac{1}{r} \right) + \frac{1}{2} \frac{\delta^2 r}{\delta \eta^s \delta \eta^r \delta \eta^m} \dot{\eta}^s \dot{\eta}^r \right\} \end{aligned}$$

The equation of motion is

$$\lambda^4 C_m^1 + \lambda C_m^6 = 0$$

Absorbing λ 's in m and using the time variable x^0 so that in the following $\dot{\xi}$ means $d\xi/dx^0$ we have

$$\begin{aligned} \ddot{\eta}^m - m \frac{\delta}{\delta \eta^m} \left(\frac{1}{r} \right) &= m^2 \left\{ \left[\eta^s \eta^s + \frac{2}{3} \dot{\eta}^s \dot{\eta}^s - 4\eta^s \dot{\eta}^s - \frac{4m}{r} - \frac{5m}{r} \right] \frac{\delta}{\delta \eta^m} \left(\frac{1}{r} \right) \right. \\ &\quad \left. + [4\eta^s (\dot{\eta}^m - \eta^m) + 3\eta^m \dot{\eta}^s - 4\dot{\eta}^s \dot{\eta}^m] \frac{\delta}{\delta \eta^s} \left(\frac{1}{r} \right) \right. \\ &\quad \left. + \frac{1}{2} \cdot \frac{\delta^2 r}{\delta \eta^s \delta \eta^r \delta \eta^m} \dot{\eta}^s \dot{\eta}^r \right\} \quad (11.67) \end{aligned}$$

The equations for the other particle are obtained by replacing $m^1, m^2, \eta, \dot{\eta}$ by $m^2, m^1, \dot{\eta}, \dot{\eta}$ respectively in the above.

It will be of some interest to find out whether the equation of a geodesic in the field of m^2 only can be cast into the form (11.67) as modified by the condition $\dot{m}^1=0$. If that is possible we will have verified that the motion of a test-particle as given by the geodesic-postulate is consistent with the motion as obtained by this new method. It is clear from (11.67) that

$$\ddot{\eta}^1 \frac{\delta}{\delta \eta^2} \left(\frac{1}{r} \right) - \ddot{\eta}^2 \frac{\delta}{\delta \eta^1} \left(\frac{1}{r} \right) \quad (11.68)$$

is independent of m . From this and from the independence of two other similar expressions of m^1 the acceleration of a particle, though not all directed radially towards the other, is found to have a transverse component which is independent of its own mass. The transverse component is a second order effect depending upon the velocity of the other particle.

In considering the relative acceleration $\ddot{\eta}^m - \ddot{\xi}^m$ one has to be alive to the fact that the equations (11.67) do not hold good in a flat space-time and that the latter possesses a small and variable curvature. The definition of relative acceleration as $\ddot{\eta}^m - \ddot{\xi}^m$ is therefore purely conventional as distant parallelism is not a feature of Riemannian space-time. The distance r as appearing in (11.67) is not the measured distance between the two particles. It must be remembered that it is the smallness of m^k compared with its radius in natural co-ordinates that makes the relativistic correction for distance usually negligible for astronomical purposes. When, however, the formulæ (11.67) are used to investigate the astronomical effects up to the second order of masses the influence of the curvature of space, as a corrective to the conventional distance, r , cannot be ignored. It has been shown by Robertson that the relativistic effect on the perihelion is the same as predicted from Schwarzschild's solution with only this difference that the mass-term stands for the combined mass in the present case. The average acceleration of the centre of gravity is found to be zero, a result, which contradicts Levi-Civita's* calculations.

The calculation of dynamical equations to a precision beyond that of (11.67) is not required by astronomers. Secondly the result would be vitiated by the increased discord between the conventional distance r and the relativistic estimate of it obtained with a due regard to the space-time curvature. It is worthwhile finding out whether Robertson's results need to be modified in view of the curvature of space-time.

The present method of moving singularities is certainly a very ingenuous one and it reminds one of the motion of line singularities determined by non-linear partial differential equations in Helmholtz's theory of vortex-motion. Up to the third order of approximation the equations of motion contain time-derivatives not higher than the second. But from the manner in which the calculations proceed it seems likely that higher time-derivatives may appear in the equations of motion. At any rate it needs to be proved, if that is true, that higher derivatives cannot come in.

*c.f. (11) and (20d).

The theory has applications even to electrodynamics*. But we have purposely avoided reference to that here, as also to the question of gravitational waves.

IV

12. NEBULÆ AND COSMOLOGY

The bricks out of which the universe is built are the extragalactic nebulae and the Central Galaxy which also is a spiral nebula like the large majority of the rest. These bricks are not just piled one over the other. Each nebula has an average diameter of about 10^4 light years and the average distance between two neighbouring nebulae is about two hundred times this average diameter. The clustering effect due to gravitation is observed in many parts of the sky, three, four or even more nebulae coming nearer together under mutual attraction. The mass of a nebula may be anything between $10^9 \odot$ and $10^{10} \odot$ where $\odot$ is the mass of the sun. As regards brightness the apparent magnitudes of the nebulae vary between +4 and +21, fainter nebulae not being observable through our telescopes. The absolute brightness†, however, of each nebula is approximately the same, the absolute magnitude being -14.2 . We may briefly explain the relation between brightness and magnitude.

Let E_m be the total quantity of energy received from a luminous source of apparent magnitude m per unit second, E_0 the corresponding energy of another source whose apparent magnitude is classed as zero and EM the quantity that would be received from the first source if it were at a standard distance of ten parsecs. Incidentally one parsec is approximately 3.258 light-years or 3.08×10^{18} cm. The apparent magnitude m is defined by

$$E_0/E_m = (2.512)^m = 10^{.4m}, \quad (12.1)$$

while the absolute magnitude M is defined by

$$E_0/EM = (2.512)^M = 10^{.4M}. \quad (12.2)$$

By the law of inverse squares

$$E_m/EM = (10/D)^2 \quad (12.3)$$

where D parsecs is supposed to be the distance of the luminous source of apparent magnitude m . Hence

$$\log_{10} D = .2(m - M) + 1 \quad (12.4)$$

The last relation is very important in the light of the fact that the absolute magnitude M of a nebula is the same in the majority

*c.f. (10).

†c.f. (14a), p. 5; note also 9a, 9b, 9c and 14b.

of the cases, its value being approximately -14.2 . The distance D of a nebula can, in principle, be determined by its apparent magnitude, using (12.4). If there is a uniform distribution of nebulae in space the total number of nebulae in a sphere of radius D parsecs will be proportional to D^3 if the space is Euclidean. Moreover, by (12.4), the faintest apparent magnitude of a nebula is found to be m in this sphere. Hence if N_m denotes the number of nebulae whose apparent magnitude does not exceed m we have

$$\begin{aligned}\log_{10} N_m &= 3 \log_{10} D + \text{const.} \\ &= .6(m - M) + \text{const.}\end{aligned}\quad (12.5)$$

When we put $m = 21$ and $M = -14.2$ in (12.4) it is clear that a nebula whose apparent magnitude is 21 is situated at a distance of the order of a hundred megaparsecs. The light of a nebula coming from such a large distance is partially obscured by the dust between the stars and the tenuous medium within which the Central Galaxy is situated. This explains why the apparent distribution of nebulae in the sky is not uniform. The crowding of nebulae near the poles of the galaxy and the gradual falling out towards the galactic plane can thus be explained.

At this stage it must be made clear that the observed counts of nebulae do not satisfy the relation (12.5). The true relation is of the form

$$\log N_m = .6(m - M - \Delta m) + \text{const.} \quad (12.6)$$

where Δm may be expressed by the relation,

$$\Delta m = 2.94 \frac{\Delta \lambda}{\lambda}, \quad (12.7)$$

in view of the fact that the whole pattern of absorption lines of a nebula is displaced towards the red so that $\frac{\Delta \lambda}{\lambda}$ is the same for all wave-lengths and for all nebulae whose distances or apparent magnitudes are the same. This phenomenon of reddening of light is a very mysterious one if it is not to be interpreted as a Doppler effect due to the recession of the nebulae. Before discussing it, along with its implications, we will concentrate our attention on the fact that the observed counts satisfy the modified relation (12.6).

On a closer examination, a correction $-\Delta m$ to the apparent magnitude is found necessary for several reasons. The obscuring material between the earth and a distant nebula certainly makes the latter appear fainter than it actually is. Two further corrections have to be made. In the first place the red-shift, which is referred to above, makes a nebula appear fainter, purely as a

kinematical effect, the cause of the phenomenon being anything. Secondly the photographic magnitude is slightly different from the bolometric magnitude, m , which we have been using above. In calculating the bolometric magnitude the total energy received from the nebula per sec. per sq. cm. is taken account of. Thus the bolometric luminosity is defined by

$$l_b = \int_0^{\infty} I(\lambda) d\lambda \quad (12.8)$$

where $I(\lambda)d\lambda$ is the energy flux between wave-lengths λ and $\lambda+d\lambda$. The photographic luminosity is given by another integral,

$$l_p = \int_0^{\infty} I(\lambda) a(\lambda) p(\lambda) d\lambda \quad (12.9)$$

where $p(\lambda)$ is the fraction that is photographically effective and $a(\lambda)$ is the fraction that is transmitted through the earth's atmosphere and the instrument. The difference between the bolometric and photographic magnitudes is given by

$$m_p - m_b = 2.5 \log \frac{l_b}{l_p} + \text{const.} \quad (12.10)$$

$$\equiv 2.5 \log p + \text{const.} \quad (12.11)$$

If the distance as measured by rigid scales in a gravitational field is D , the bolometric luminosity is given by

$$l_b = \frac{\text{const.}}{D^2} \cdot \frac{1}{(1+z)} \quad (12.12)$$

where z is the Doppler displacement. Hence

$$l_p = \frac{\text{const.}}{D^2} \cdot \frac{p}{(1+z)} \quad (12.13)$$

Now note that

$$m_p = 2.5 \log \frac{1}{l_p} + \text{const.} \quad (12.14)$$

Therefore,

$$\log_{10} D = .2 [m_p - 2.5 \log_{10} (1+z) + 2.5 \log_{10} p] + \text{const.} \quad (12.15)$$

For a nebula situated at $D=10$, the Doppler displacement would be negligible and the integrals (12.8) and (12.9) would bear a different ratio, P . In this case,

$$1 = .2 [M + 2.5 \log_{10} P] \quad (12.16)$$

Subtracting (12.16) from (12.15) we have

$$\log_{10} D = .2 [m_p - 2.5 \log_{10} (1+z) - K - M] + 1 \quad (12.17)$$

where K is called the bolometric correction. The kinematical

correction due to the Doppler effect is given by the term $-5 \log_{10} (1+z)$. In deducing (12.12) use was made of the relation

$$E \lambda = \text{const.} \quad (12.18)$$

for a photon, E being the energy. The effect of an increase in λ by $\Delta \lambda$ is to diminish the energy in the ratio $(1+z) : 1$. When the fact of recession is used we must account for the diminution in the number of photons arriving. That makes the formula for l_b ,

$$l_b = \frac{\text{const.}}{D^2} \frac{1}{(1+z)^2} \quad (12.19)$$

The corresponding change in the formula (12.17) would lead to

$$\log_{10} D = .2 [m_p - 5 \log_{10} (1+z) - K - M] + 1 \quad (12.20)$$

In evaluating K the surface temperature of a nebula is assumed to be of the order of 6000°C .

A study of the red-shifts of the nebulae gives the empirical relation

$$z \equiv \frac{\Delta \lambda}{\lambda} = k D \quad (12.21)$$

where D is the distance of the nebula whose shift is z and k is a constant of proportionality. Using this value of z in (12.17) we find that

$$\Delta m = 2.5 \log_{10} (1+z) + K = \frac{3 \Delta \lambda}{\lambda}, \text{ approximately.} \quad (12.22)$$

This value of Δm agrees very closely with the value required for experimental confirmation as given in (12.7). The immediate inferences are that space-time is flat, that there is a uniform distribution of nebulae in space, that intergalactic space is more or less transparent and that light rays lose energy in some unaccountable manner as they travel through space and in the regular manner as given by (12.21). The nebulae may be subject to small proper motions but their Doppler effects are not appreciable enough to affect the above conclusions.

The inferences made above, following the agreement between (12.22) and (12.7) are not acceptable because of the mystery that remain unsolved regarding the spectral shift. Rather than look for an entirely new physical principle to save the situation one finds it more satisfying to attribute the shift to recession and decide if the situation can thus be explained.

When the spectral shift is interpreted as a Doppler effect the formula (12.20) holds good. Now the value of Δm becomes $\frac{4 \Delta \lambda}{\lambda}$ approximately and this is certainly not in agreement with

observation. Another difficulty also arises. The velocity of recession v as given by

$$v = c \frac{\Delta \lambda}{\lambda} \quad (12.23)$$

is found to attain the value of the velocity of light c for nebulae at a distance of 1860 million light years. This not only makes the radius of the observable universe small; but it also means that most of the nebulae were in our neighbourhood 1860 million years ago. The beginning of recession is too recent compared to the age of the stars of the galaxy determined by other criteria. To meet the situation it is assumed that the space is curved. The relation (12.5) needs to be modified now. Following Tolman we may take the line-element

$$ds^2 = -e^{-\psi(t)} \left[\frac{dr^2}{1 - kr^2/R_0^2} + r^2(d\theta^2 + \sin^2\theta d\phi^2) \right] + dt^2 \quad (12.24)$$

to represent the space-time of the universe. The number of nebulae within a distance of D parsecs is N and, if $k=1$,

$$\begin{aligned} N &= \text{const.} \int_0^D \frac{r^2 dr}{(1 - r^2/R_0^2)^{1/2}} \\ &= \text{const.} R_0^3 [\sin^{-1}x - x\sqrt{1-x^2}] \\ &= \text{const.} D^3 [\sin^{-1}x - x\sqrt{1-x^2}]/x^3 \end{aligned} \quad (12.25)$$

$$\text{where } x = D/R_0, \quad R_0 > D. \quad (12.26)$$

Using (12.17) in (12.25)

$$\log_{10} N = 0.6 (m_c - \Delta \lambda / \lambda + c_v) + \text{const.} \quad (12.27)$$

$$\text{where } m_c = m_p - 2.5 \log_{10} (1+z) - K \quad (12.28)$$

$$\text{and } c_v = \frac{10}{6} \log_{10} \left[\frac{3}{2x^3} \left\{ \sin^{-1}x - x\sqrt{1-x^2} \right\} \right] \quad (12.29)$$

The symbol m_c stands for the corrected magnitude. It is obvious from (12.27) that for agreement with observation,

$$\Delta \lambda / \lambda = c_v. \quad (12.30)$$

This relation gives us the value of R_0 . The relation (12.21) no longer holds good. We have instead

$$\begin{aligned} z = \frac{\Delta \lambda}{\lambda} &= kR_0 \sin^{-1}x = \frac{kD}{x} \left(x + \frac{x^3}{6} + \dots \right) \\ &= kD + \frac{kD}{6} x^2, \text{ approximately.} \end{aligned} \quad (12.31)$$

A more general formulæ for z would be

$$z = kD - lD^2 + \left(\frac{k}{6R_0^2} + \frac{1}{3}kl + m \right) D^3 \quad (12.32)$$

where k, l, m are defined in the expansion,

$$g(t) = 2(kt + lt^2 + mt^3 + \dots) \quad (12.33)$$

We get $R_0 = 4.7 \times 10^8$ light-years, (12.34)

when use is made of Hubble's empirical relation*,

$$\log_{10} N_m = 0.6m_c - 4.437 \quad (12.35)$$

to compare with $\log_{10} N_m = 0.6(m_c - \Delta \lambda / \lambda + c_v) - 4.391$ (12.36)

The empirical formula for the Doppler shift is

$$z = 5.37 \times 10^{-10} D + 2.54 \times 10^{-19} D^2, \quad (12.37)$$

which may be compared to (12.32). Hubble, who has been largely responsible for the observational findings of the theory, closes his remarks with a note of pessimism and uncertainty at the end of his book. "The Observational Approach to Cosmology," : "Larger telescopes may resolve the question, or theory may be revised to account for the new data. But with regard to relativistic cosmology in its present form, and the observations now available, the conclusion can be stated quite simply. Two pictures of the universe are sharply drawn. Observations, at the moment, seem to favour one picture, but they do not rule out the other. We seem to face, as once before in the days of Copernicus, a choice between a small, finite universe, and a universe indefinitely large plus a new principle of nature."

The conclusion drawn by Hubble needs to be modified in one respect. Granted that the space-time of the universe is of the form (12.24) it does not follow that the universe must necessarily be finite; a hyperbolic universe is also possible and from the elegant analysis of the question as made by McVittie it seems doubtful if the observational data would ever help us in deciding the precise form of the world-model. We will briefly sketch McVittie's treatment of the question here.

It is obvious from (12.24) that if $k=0$ the space is conformal to a flat one; If $k=+1$ it is spherical and finite and if $k=-1$ it is hyperbolic and infinite in extent. The distance D of a nebula satisfies the relation,

$$\log_{10} D(1+z) = .2(m - M - K) + 1 \quad (12.38)$$

which has been expressed differently in the formula (12.20). Assume $g(0)=0$ so that the radius of the model is R_0 at $t=t_0$. A ray of light leaving a nebula at $t=t_1$ will reach the observer at time $t=0$ so that

$$(1+z) = e^{-\frac{g}{2}(t_1)} \quad (12.39)$$

* *c.f.* (9c), p. 65.

Since the path of a light-ray is a null-geodesic

$$\int_0^D \frac{dr}{(1 - kr^2/R_0^2)^{1/2}} = \int_{t_1}^0 e^{-\frac{g}{2}(t)} dt \quad (12.40)$$

Neglecting higher powers of D/R_0 than the second,

$$D = \frac{2}{g'_0} z + 2 \frac{g''_0}{g'^2_0} z^2 + \frac{1}{g'^3_0} \left[-\frac{2}{3} g''_0 + 4 \left(\frac{g''_0}{g'_0} \right)^2 - \frac{4}{3} \frac{g'''_0}{g'_0} - \frac{4k}{3R_0^2} \right] z^3 \quad (12.41)$$

where g'_0 means $(dg/dt)_{t=0}$ etc. Substituting for D in (12.38) we get

$$\log z = 0.2 \left[m - \left\{ k + \frac{5}{E} \left(1 + \frac{g''_0}{g'^2_0} \right) z + \frac{5c}{3E} z^2 \right\} \right] + 1 - 0.2 M + \log(g'_0/2) \quad (12.42)$$

$$\text{where } C = \frac{9}{2} \left(\frac{g''_0}{g'^2_0} \right)^2 - \frac{g''_0}{g'^2_0} - \frac{2g''_0}{g'^2_0} - \frac{3}{2} - \frac{2}{g'^2_0} \cdot \frac{k}{R_0^2} \quad (12.43)$$

$$\text{and } E = \log_e 10 = 2.303 \quad (12.44)$$

The number of nebulae N within a sphere of radius D is proportional to

$$\int_0^D \frac{r^2 dr}{(1 - kr^2/4R^2)^{1/2}} \quad (12.45)$$

$$\text{Hence } \log_{10} N = 0.6 \left[m - \left\{ k + \frac{5}{E} z - \frac{5}{2E} \left(1 + \frac{1}{5} \frac{k}{R_0^2} \frac{4}{g'^2_0} \right) z^2 \right\} \right] - 0.6 M + \text{const.} \quad (12.46)$$

The empirical form of the relation (12.42) is

$$\log z = 0.2 (m - 3z) - 4.707 \quad (12.47)$$

while the empirical form of (12.46) can be either taken as

$$\log_{10} N = 0.6 (m - 2.95z) - 4.437 \quad (12.48)$$

$$\text{or as } \log_{10} N = 0.6 (m - 3.43z + 2.01z^2) - 4.426 \quad (12.49)$$

If we choose (12.48) our formulae give a hyperbolic universe,

$$k = -1, R_0 = 2.58 \times 10^8 \text{ parsecs} \quad (12.50)$$

and the value of K corresponds to nebular radiation of a colour temperature exceeding 7500°C . If we choose (12.49) the theoretical formulae give a finite spherical universe,

$$k = 1, R_0 = 3.11 \times 10^8 \text{ parsecs}, \quad (12.51)$$

while the value of K corresponds to nebular radiation of a colour-temperature slightly less than 7000°C . The statistical data connecting m , $\log N$, z are very meagre and they permit the

formulation of either of the two relations (12.48) and (12.49). When we see, on one hand, the number of difficulties encountered in getting reliable observational data concerning m , N and z and how, on the other hand, a suitable difference in alternative polynomial representations of the data leads to different world-model we wonder whether the nebular method will point unequivocally to a definite relativistic world-model before we become vastly richer in our information of the nebulae.

In the above we have considered two distinct features of the nebulae. Our considerations started with the assumption that the nebular distribution is fairly uniform in space. The assumption pleases our æsthetic sense but there is no reason why it should be true and there are observers who do question the validity of the assumption. If the assumption is right—and it does look plausible in the light of Hubble's work—we have first to account for the observed departure from the postulated law of uniform distribution. The complication caused by the fact that the absolute magnitudes of nebulae are scattered about -14.2 is smoothed out by the direct assumption that each nebulae has the same corrected magnitude.

It may, however, be a matter for investigation whether this assumption does not aggravate our difficulties. But that is incidental in the present discussion. The next difficulty encountered is regarding the red-shift of the nebulae. If the red-shift does not mean recession a purely kinematical explanation of the distribution as observed can be given. One's mind is, however, uneasy on the score that the cause of the red-shift remains undetermined. The alternative was to treat the red-shift as due to recession and explain the distribution and motion by the postulates (A), (B), (C) of relativity and an additional uniformity postulate. The situation raised by the work on nebulae does not necessarily call for the use of Einstein's gravitational equations involving $\rho_{\mu\nu}$ and $T_{\mu\nu}$. These equations are used for speculations regarding the energy and pressure in the universe and the dynamical evolution; and we have already questioned the logical validity of this procedure. Such speculations may be made in accordance with the set of equations of any gravitational theory. Milne and McCrea* have shown how the dynamical state and evolution of a world-model can be found out by using Newton's law of gravitation. It is interesting to see in their investigation that Newton's law leads to equations which are mathematically of the same form as Einstein's equations and that what is called the inherent

*c.f. (13a) and (15a).

curvature of space by relativists appears here as the excess or deficiency of the square of the velocity of a particle, away from its neighbours, over the square of the parabolic velocity of escape. The working out of the problem is mathematically interesting but it is vitiated by the logical invalidity of the procedure. Newton's law of gravitation rests on his first law of motion, which implies a substratum of particles in uniform relative motion. It is not logical, therefore, to assume a substratum filled with an infinite dust-cloud of particles which attract each other according to Newton's law.

We have learnt how the data of nebulae lead to an expanding universe, the time-scale of the phenomenon being of the order of 10^{10} years. This scale is so short that the expansion no longer appears as the most primitive and fundamental activity of the universe. It must be mentioned that some authorities do consider the time-scale long enough to account for stellar evolution the evolutionary processes being accelerated in the beginning. Secondly, relativists believe in an objective curved space of the universe the curvature of which is to be determined by the nebular data. The space in physics, as well as time, must be determined by the observer's measurements. The measurements leave the freedom of defining distance to the observer and there is no obvious reason, therefore, why the space of physics should be necessarily curved. Whatever conclusions are reached, regarding the curvature of the universe and the time scale, are valid only with reference to the particular representation of relativity, which will have to be given up, when the postulates and hypotheses of the theory fail to accommodate new facts of experience. Thirdly, the velocities given by the Doppler shift regularly increase with the distance and are quite large. From the theoretical relation

$$\log_{10} D = 0.2(m - M) + 1 \quad (12.4)$$

and from the empirical relation of Hubble and Humason, viz.,

$$\log_{10} cz = \log_{10} v = 0.2m + 0.507 \quad (12.52)$$

we have $\log_{10}(v/D) = 0.2M - 0.493 \quad (12.53)$

Putting $M = -14.2$ and $D = 10^6$ parsecs we obtain

$$v = 465 \text{ Km./sec. per megaparsec.} \quad (12.54)$$

There is considerable uncertainty about the empirical relation (12.52) and ~~it may~~ ^{we may} assume even a greater value.* In view of all this it is worthwhile examining whether a purely kinematical

*c.f. (14a), p. 10.

explanation cannot be given of the observed distribution and recession of nebulae starting from fundamental ideas of space and time. The recession is a type of motion essentially different from the gravitational motion, specimens of which are provided by the solar system and stellar systems as well. It is possible that some motions, for the explanation of which we turn to gravitation, can be understood as purely kinematical phenomena. A primitive kinematical explanation of such an unusual phenomenon as general scattering is bound to affect the laws of mechanics. Moreover these modified laws will have to be in harmony with all other motions that are commonly called gravitational.

In order to emphasize the fact that the velocities of recession are purely kinematical effects we may mention what is not usually appreciated and clearly brought out, *viz.*, that the velocity of a nebula as given by the geodesic-postulate is different from the velocity indicated by the red-shift. For a line-element of the form (12.24) nebulae may be supposed to be permanently at rest at points (r, θ, ϕ) in which case the geodesic-postulate gives, what is consistent with the above supposition,

$$\frac{dr}{ds} = \frac{d\theta}{ds} = \frac{d\phi}{ds} = 0, \quad \frac{dt}{ds} = 1; \quad (12.55)$$

yet the Doppler effect is non-zero and a velocity of recession is inferred because the distance of the nebulae changes with respect to the observer's metre rod. It is curious to find that when the relativist comes to the problem of the world at large his representation involves an absolute space of a definite curvature-function and an absolute time.

Assuming that the nebulae have been at rest at points (r, θ, ϕ) , since the epoch of creation, $t = t_0$, the world-map at any instant, as given by (12.24) shows that the total number of nebulae within a sphere of radius D will always be the same. From the observer's point of view what is of interest is whether the total number of nebulae seen at a time is the same. It is obvious that the two need not be identical because of the finiteness of the velocity of light. If a light-signal leaves the nebula at r, θ, ϕ at local time t' and arrives at the observer at his time t then since $ds = 0$ along the path,

$$\int_{t'}^t \frac{1}{e} g dt = \int_0^r \frac{dr}{(1 - kr^2/R_0^2)} \quad (12.56)$$

For two neighbouring light-signals, from the same nebula to the same observer,

$$0 = \int_t^{t'} \frac{1}{e} g dt - \int_{t'+dt'}^{t'+dt} \frac{1}{e} g dt \quad (12.57)$$

$$\text{and so} \quad s = \frac{dt}{dt'} = e^{\frac{1}{2}g(t') - \frac{1}{2}g(t)}$$

Hence from (12.56) and (12.57) we get a relation of the form

$$r = f(s, t) \quad (12.58)$$

The total number of nebulae observed with the Doppler shift variable s varying between ∞ and 1 is

$$N = \text{const} \int_1^{\infty} \frac{f^2 f' ds}{(1 - kf^2/R_0^2)^{1/2}} \quad (12.59)$$

The value of N does in general vary with time. The reason is that when the integration is performed for N the limits from 1 to ∞ for s do not correspond to the same limits for r at all times, because of the relation (12.58). In the world-picture of the observer, therefore, in general, either new nebulae will continue to appear or some of the observed nebulae will continue to fade away; and he will have either the impression of new matter being created or of an annihilation of matter. Either experience is sufficiently strange and startling and whether one discards or not a world-map which presents such a picture, the importance of examining some of the conceptual elements in general relativity, from the observer's view-point, cannot be denied. In the world-picture presented by Milne there is always the same number of particles and one can trace it to the constancy of relative motion of fundamental observers in his theory.

To use again another phrase of Milne's the formula (12.24) gives obviously the "public space-time" of the universe. t is the public time, being the same all over the world and the cross-section $t = \text{const}$, gives at any instant the public space. In the Newtonian theory there is no distinction between the public space-time and the private space-time and, in general relativity it follows from Robertson's work that the same holds good; but in either theory the distinction between a world-map and a world-picture does persist.

In the relativistic treatments of the nebulae and the world-structure the nebular distribution is assumed to be uniform in space. Milne's treatment gives a law of distribution of nebulae

in terms of the Doppler shift variable $s=(1+z)$, viz.,

$$dN \propto \frac{(s^2-1)^2 ds}{4s^2} d\omega \quad (12.60)$$

where dN is the number of nebulae inside a solid angle $d\omega$ and with Doppler shifts lying between s and $s+ds$. It is important that N is not a function of time which means that the counts of the nebulae in terms of the shifts will always lead to the same result, $N(s)$. The law (12.60) is fairly in conformity with observation. It does suggest an increase in dN/ds with the Doppler shift which is qualitatively in agreement with observation. At any rate we cannot reject (12.60) until we compare it with the results of a larger number of observations. As regards the redshift, it is supposed to be due to recession and the theoretical law of recession is

$$dr/dt=r/t \quad (12.61)$$

r being the radial distance, t the time since the epoch of creation, $t=0$ and r the distance of the nebula from an observer. It follows from (12.61) that

$$\frac{d^2r}{dt^2}=0; \quad (12.62)$$

the velocity of recession is constant and proportional to the distance.

We will now give an account of Milne's philosophy of space-time and of the important implications and results of the theory.

13. MILNE'S THEORY

Milne starts with hypothetical observers equipped with a theodolite and a time-consciousness to construct their own space-time by their measurements. Realizing the difficulty of defining a rigid rod the observers define space by making time-observations at themselves. The difficulty of defining equal intervals of time is also surmounted in an ingenious manner.

The space-time continuum is supposed to be inhabited by a number of particle-observers. It is the mode of measurements adopted by the observers and the measurements themselves that will give a structure to the space-time. The concept of uniform relative motion is replaced by that of kinematical equivalence which is more fundamental. Two observers A and B are said to be kinematically equivalent when the totality of the observations that A can make on B are described by A in the same manner as B would describe his observations on A. Suppose that A sends a

light-signal to B at his own time t_1 and the signal, on being reflected back from B, reaches A at his time t_2 . The epoch when the light-signal reaches B may be described by B as t'_B according to his own clock but A describes it by the epoch $\frac{1}{2}(t_1 + t_2)$ and the distance of B at that instant is reckoned as $\frac{1}{2}c(t_2 - t_1)$ where c is a conventional positive constant, the same being chosen by all observers. A can also determine the Doppler effect dt_2/dt'_B for B. Similar observations can be performed by B on A and the notion of kinematical equivalence gives us the working of one observer's clock in terms of the working of the other observer's. In order that the synchronization of the clocks may be complete all the clocks are supposed to have a common origin $t=0$ when all the observers are together; further the observers themselves are supposed to be statistically equivalent. A and B are statistically equivalent when A's description of all the particles, of which A and B are members, is in the same statistical terms as B's description of the same. These conditions not only synchronize the clock they give the distribution function of the observers and also their velocity distribution. These functions, already referred to in (12.60) and (12.61) are identified as the function giving the distribution and recession of the spiral nebulae. Equation (12.62) shows that the velocities of recession with respect to any one are constant in magnitude and direction. There is no loss of generality in assuming that the fundamental particle-observers have uniform relative motion; for it has been shown by Whitrow that it is a mere matter of appropriate regraduation of clocks to transform relative acceleration into uniform relative velocities. The fundamental particles with which the fundamental observers are associated constitute the substratum of the smoothed-out universe of Milne's theory. In the subsequent development of the theory the guiding principle is the cosmological principle which says: "The development of the universe appears to be the same for each observer of an equivalent set, everyone of whom assigns co-ordinaters by the same method."

The equations giving the acceleration of a free particle* which is one of a statistical set of particles, satisfying the cosmological principle, are of the form

$$\frac{dV}{dt} = \frac{Y}{X} (P - Vt) G(\xi) \quad (13.1)$$

* c.f. (33a); (33b) is a very important paper which brings out the distinguishing characteristics of Milne's theory. (20b) is equally important. For purely gravitational implications and results of Milne's theory reference must be made to his own recent papers.

where $P=(x, y, z)$, $V=(u, v, w)=\left(\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}\right)$ (13.2)

$$X=t^2-\frac{x^2+y^2+z^2}{c^2}, \quad Y=1-\frac{u^2+v^2+w^2}{c^2} \quad (13.3)$$

$$\xi=\frac{Z^2}{XY}, \quad Z=t-\frac{ux+vy+wz}{c^2} \quad (13.4)$$

and $G(\xi)=-1-\frac{C}{(\xi-1)^{3/2}\Psi(\xi)}$ (13.5)

The constant C and the function Ψ are arbitrary. The analogue of Newton's first law is obtained from $C=0$. Thus,

$$G(\xi)=-1, \quad (13.6)$$

sums up the influence of the substratum on a free particle. It is the other term in $G(\xi)$ that explains the gravitational effect and particularly the inverse-square law of gravitation.

If the clocks of all fundamental observers are regraduated by the law of transformation

$$\tau=t_0 \log(t/t_0)+t_0 \quad (13.7)$$

where t_0 is the time elapsed since all the fundamental observers were together a series of interesting consequences follow. τ is invariant for all fundamental observers and is found to play the role of the Newtonian absolute time. For the description of dynamical phenomena inside a spiral nebula the time τ seems to be appropriate though the spiral structure itself can be explained only with the t -scale. From the equations of motion of a pair of particles it is clear that the orbits which appear as equiangular spirals in the t -dynamics are Keplerian in the τ -dynamics. If indeed the time-scale of the nebular phenomena is different from the time-scale of the stellar and planetary phenomena the difficulty created by the small period of expansion, viz., $t=2 \cdot 10^9$ years can now be satisfactorily disposed of. The time-co-ordinate t and the Euclidean space represent an observer's private space-time while the time τ and a hyperbolic static space appear as the public space-time. The connection between the two space-times is given by

$$ds^2=dt^2-\frac{1}{c^2}(dr^2+r^2d\theta^2+r^2\sin^2\theta d\phi^2) \quad (13.8)$$

$$=e^2(\tau-t_0)/t_0 \left[d\tau^2-\frac{1}{c^2} \left\{ d\lambda^2+(ct_0)^2 \sin^2 h^2 \frac{\lambda}{ct_0} (d\theta^2+\sin^2\theta d\phi^2) \right\} \right] \quad (13.9)$$

The light received from nebulae shows us a red-shift and one concludes from this that atoms keep the time t and not τ . The gravitational constant which is a function of time on the t -scale is a constant number on the τ -scale. The angular momentum is conserved on the τ -scale but it is found to increase with time when expressed as a t -measure. The genesis of angular momentum in celestial systems has not been successfully accounted for and Milne's result in this connection seems to be a very promising one.

One feature of Milne's results on the t -scale has been emphasized by Dirac* who has recently formulated a new cosmological principle. The present epoch or age of the universe appears explicitly in the radius of the universe, in the gravitational constant γ and in a number of other dynamical features. According to Dirac's cosmological principle "Any two of very large dimensionless numbers occurring in Nature are connected by a simple mathematical relation, in which the coefficients are of the order of unity." If this is true the present epoch t_0 must appear in many of the dimensionless numbers which come out as constants in the present-day physics.

Critics of Milne's theory have severely criticized it for its two time-scales. They should like to know whether the Astronomer Royal's time is τ or t . On theoretical grounds it is difficult to answer this question at present because

$$\frac{d\tau}{dt} = \frac{t_0}{t} \quad (13.10)$$

and the value of $d\tau/dt$ at $t=t_0$ is unity. It is only when we come to the problems of cosmology that we notice the difference in the two time-scales. If we use the τ -scale in discussing the recession of the nebulae we find that there is no recession, that the universe is infinite and that the time-origin is shifted to $\tau = -\infty$. These details of the world-structure are radically different from what we have already described, using the t -scale, as suggested by the observed red-shifts.

In fine one remark may be made regarding the gravitational constant. Are we to suppose that it is conditioned by the matter and motion of our own galaxy as in Milne's theory? In that case there is probably a different gravitational constant for each nebula or island universe. Or, are we to suppose that the world-structure is responsible for its value? In either case we do not see how Einstein's equations, which involve the Newtonian value of the

*cf. (3).

constant, can be used with any justification for determining the world-structure. In using his cosmological principle and the equations of relativity to find the curvature of space-time Dirac has suitably modified the gravitational constant appearing in the latter.

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EFFUSION PHENOMENA AND QUANTUM STATISTICS

By

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In view of the numerous applications of the new quantum statistics to physical problems, it may be worth while to investigate the effusion of energy of a gas obeying Fermi-Dirac statistics. The calculation is simple and runs on the usual lines. It is found that for a degenerate gas, degenerate in the sense of Fermi-Dirac statistics, the energy effusing out per second per unit area is given by

$$E_{deg} = \frac{3}{128} \frac{h^3}{\pi m^3} \cdot n^3 \quad \dots \quad \dots \quad (1)$$

for the completely non-relativistic case, and

$$E_{deg}^R = \frac{3}{16} c^3 h \left(\frac{3}{4 \pi g} \right)^{1/3} n^{4/3} \quad \dots \quad \dots \quad (2)$$

for the completely relativistic case, where n is the number of particles (each of mass m) per unit volume, g the weight factor (equal to 2 for electrons), c the velocity of light, and h is Planck's constant.

In the case of non-degeneracy it is found that the rate of effusion of energy is given by

$$E = \frac{nkT}{2} \sqrt{\frac{8kT}{m\pi}} \left[1 - \frac{3}{8y} + \beta \frac{A_0}{8} (2\sqrt{2}-1) \right] \quad \dots \quad (3)$$

for the non-relativistic case, where

$$A_0 = \frac{nh^3}{g(2\pi mkT)^{3/2}} \quad (\text{D. S. Kothari, Proc. Nat. Inst. Sci. India, 1938, 4, 69}) \text{ and } y = mc^2/kT$$

k being Boltzmann's constant and T the absolute temperature. Expression (3) reduces to the simple formula for a classical perfect gas

$$E = \frac{nkT}{2} \sqrt{\frac{8kT}{m\pi}} \quad \dots \quad \dots \quad \dots \quad (4)$$

when $A_0 \rightarrow 0$ and $y \rightarrow \infty$.

For the relativistic case ($y \ll 1$), the energy effusing out is found to be given by

$$E = \frac{3}{4} n k T c \left[1 - \frac{y}{3} + \frac{\beta A_0^R}{16} \dots \dots \right] \quad \dots (5)$$

where $A_0^R = \frac{n}{8 \pi g} \left(\frac{ch}{kT} \right)^3$ (D. V. Gogate, Phil. Mag., 1938, 25, 694)

and $\beta = +1$ for F. D. statistics and -1 for B. E. statistics. For the completely relativistic case ($y \rightarrow 0$) and for a completely non-degenerate system, equation (5) reduces to

$$E^R = \frac{3}{4} n k T c \quad \dots \quad \dots \quad \dots \quad \dots (6)$$

If the asymptotic formulæ contained in the equations (1), (2), (4) and (6) are represented graphically by plotting $\log E$ against $\log n$, it is at once seen that :—

- (a) In the case of a degenerate gas, the effusion of energy is greater than in the case of a non-degenerate (classical) gas at the same temperature.
- (b) the effusion of energy of a degenerate gas, is very large compared with what would be computed for a classical gas at the same temperature and concentration.
- (c) the effusion of energy of a classical gas is very large compared with what would be computed for a degenerate gas at the same temperature and concentration.

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A NOTE ON THE EXPERIMENTAL STUDY OF CUMULUS CLOUDS

By

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The rising up and the growth of a Cumulus cloud is somewhat similar to the motion of a fluid mass having a smaller density than its surrounding. In the beginning, the lighter mass of fluid could be kept at the bottom of a heavier fluid with the help of solid boundaries, and then released to move up under the influence of gravitational forces. This method is very inconvenient, as the removal of the solid boundaries produces a disturbance in the fluid. However, it could be conveniently arranged that the heavy fluid is allowed to sink in a lighter one. This then would simulate the inverted way in which a Cumulus cloud would rise from the surface of the earth.

It is known that the Cumulus cloud rises to a certain height in the atmosphere and then spreads to a certain extent in an horizontal direction. At this place there is a sudden change of density and the layer there is known as "Inversion Layer". In our laboratory experiment, this layer is represented by a column of salt solution of greater density than that of the falling fluid. When this layer is at the bottom of the tank, it is in a stable position and remains there without mixing with the water above it. The falling fluid now instead of striking the solid bottom of the tank, strikes this layer and after penetrating it to a certain extent, spreads against it.

Fig. 1 gives a diagrammatic sketch of the apparatus used for the study of the above-mentioned phenomenon. A rectangular tank with the glass sides (162 Cm. long, 52 Cm. wide and 58 Cm. high) was used in the experiments. A cylindrical dish of thin walls and capable of rotation about the cylinder axis, was fitted at the top of the tank as shown in Fig. 1.

The tank was filled with a strong salt solution to a height of about 10 Cm. and then pure water was allowed to fill the tank without disturbing the layer formed by the salt solution at the bottom. The cylindrical dish was filled with a coloured salt-solution whose density was less than that of the layer at the bottom but greater than that of pure water. The densities were accurately

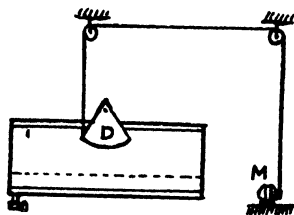


Fig. 1

determined with a specific gravity balance, capable of accurate measurement correct to the fourth place of decimal.

A clock driven by a regulated mechanical motor was mounted on the tank. The dial had hundred divisions marked in white on dark background and the pointer was also pointed white. It was so arranged as to get the time for one complete revolution of the pointer to be one second ; thus we could read $1/100$ of a second very easily. The clock was started just before the liquid was allowed to fall down from the dish D and the motion of the falling fluid was photographed along with the clock, with a cine-camera. The field was illuminated by high power electric lamps kept behind a ground glass screen.

The measurements were made by projecting the film pictures on a big sheet of graph-paper and marking the positions of the fluid at different intervals. It is found from these pictures that the vertical distance travelled by the falling fluid is smaller than that produced by an acceleration $\frac{\rho_1 - \rho_0}{\rho_1} g$, where ρ_1 is the density of the

falling fluid, ρ_0 the density of pure water and g the acceleration due to gravity. Fig. 2 shows the actual distance travelled by the falling fluid at any given time measured from the start of the motion

The curve $h = \frac{1}{2} \left(\frac{\rho_1 - \rho_0}{\rho_1} \right) g t^2$ is plotted for the comparison of the

actual motion of the cloud with that expected under ideal condition *i.e.* without any resistance. To get an idea about the motion of the falling fluid when it meets the layer at the bottom, the position of this layer is shown in the figure by dotted line. This corresponds to altitude measurement of a cumulus cloud in the course of time.

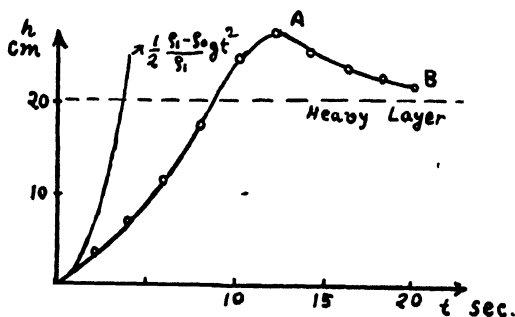


Fig. 2

Fig. 2 shows that the two curves coincide in the immediate neighbourhood of the origin. This means that the acceleration of the falling fluid in the beginning is $\frac{\rho_1 - \rho_0}{\rho_1} g$, same

as in an ideal case. As the velocity increases, the resistance offered by the surrounding fluid increases and the actual motion becomes much slower than the one produced by the acceleration $\frac{\rho_1 - \rho_0}{\rho_1} g$. The

kinetic energy of the falling fluid at the time it reaches the layer at the bottom of the tank, is destroyed by the penetration in this layer against an acceleration $\frac{\rho_2 - \rho_1}{\rho_1} g$. Within this layer the

fluid having a smaller density is in an unstable condition, and as a result of this, it spreads against this heavy layer. (See Fig. 3).

Experiments were also made to study the motion of a heavy fluid kept in an unstable condition within a lighter fluid. The initial form of the unstable fluid was made to resemble the form of the falling fluid when it attains its maximum vertical distance in the heavy layer. The motion is identical in all planes parallel to the plane of the glass walls of the tank and so the motion could be treated as two-dimensional in the plane of the picture. The initial form could be represented by a flat parabola in the plane of symmetry. The results of different experiments corresponding to different portions of the curve represented in Fig. 2 are not given, but it can be mentioned here that the results agree with the motion represented in Fig. 2.

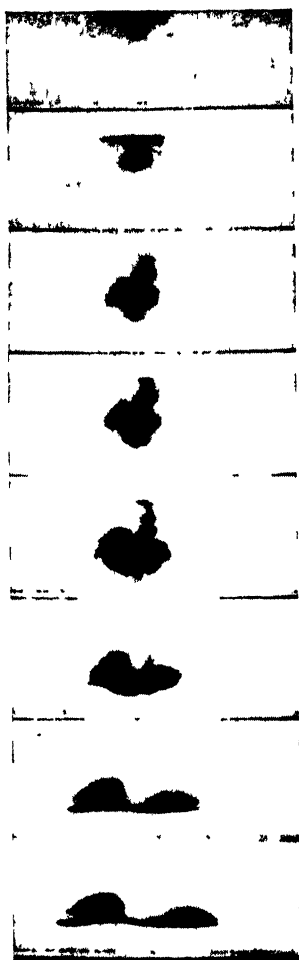


Fig. 3

•The theoretical nature of the motion of the fluid spreading against the heavy layer can be briefly given here. The initial form of the fluid that spreads can be taken as a flat parabola. Let ρ_1 be the density of the fluid in an unstable condition and ρ_0 that of the fluid surrounding it, then as a first approximation it

could be assumed that the motion is only due to the statical pressure difference. The parabola is taken to be very flat so that the vertical velocities could be neglected in comparison to the horizontal ones. Fig. 4 gives the symbols used to denote the

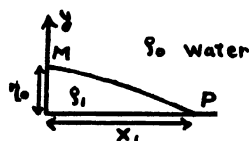


Fig. 4

maximum vertical height and the maximum horizontal range of the parabola at any instant *i.e.* at $t=t$. At the beginning of the motion $\eta_0 = h_0$ $x_1 = x_0$. The equation of the parabola could be written as

$$y = \eta_0 - \beta_0 \frac{x^2}{2} \quad (1)$$

where η_0 and β_0 are functions of time. Now if we assume the motion to be a potential one, we can write the velocity potential as

$$\phi = \frac{x^2 - y^2}{2} f(t) \quad (2)$$

where $f(t)$ is another function of time. We now get the velocity components as

$$\left. \begin{aligned} u &= \frac{\partial \phi}{\partial x} = x \cdot f(t) \\ v &= \frac{\partial \phi}{\partial y} = -y \cdot f(t) \end{aligned} \right\} \quad (3)$$

In addition we know that at M (Fig. 4) $u=0$ and $v = \frac{d\eta_0}{dt} = -\eta_0 f(t)$,

and at P, $v=0$ and $u = \frac{dx_1}{dt} x_1 f(t)$. With these conditions we can

eliminate $f(t)$ and correlate η_0 and x_1 and thereby evaluate β_0 . The equation of the parabola now assumes the form

$$y = \eta_0 - \eta_0^2 \frac{x^2}{c^2} \quad (4)$$

where $c = x_0 h_0$.

The ratio $\frac{\eta_0}{h_0}$ or $\frac{x_0}{x_1}$ gives us an idea about the spreading of the fluid, as the value of this ratio indicates the value of the maximum height or the maximum range at any time in terms of the initial condition. To get this ratio we write down the energy equation of the unstable fluid.

$$\begin{aligned} \text{The potential energy} &= -2g (\eta_1 - \eta_0) \int_0^{x_1} dx \int_0^{\eta_0} y dy \\ &= -\frac{8}{15} g (\eta_1 - \eta_0) \eta_0 c. \end{aligned}$$

$$\text{The kinetic energy} = \eta_1 \int_0^{x_1} dx \int_0^{\eta_0} u^2 dy = \frac{2}{15} \eta_1 c^2 \frac{f(t)^2}{\eta_0^2}$$

In the second expression v^2 is neglected in comparison to u^2 . One can also evaluate $f(t)$ from the boundary conditions for u and v then we get $f(t) = \frac{\eta_0'}{\eta_0}$ and $f(t)^2 = \frac{\eta_0'^2}{\eta_0^2}$. With these values the energy equation becomes :—

$$\frac{2}{15} g_1 c^2 \frac{\eta_0'^2}{\eta_0^2} - \frac{8}{15} g c (g_1 - g_0) \eta_0 = \text{const.} \quad (5)$$

The constant can be evaluated with the conditions that at $t=0$; the K.E.=0, and $\eta_0 = h_0$ then we get the constant to be equal to

$$-\frac{8}{15} g c (g_1 - g_0) h_0.$$

Integrating and writing the value of the constant of integration with the help of initial conditions, we get a relation for η_0 and h_0 with respect to time. This relation which is not in an explicit form, could be written in such a way as to get both the sides of the equation (6) dimensionless.

$$\frac{\sqrt{(h_0 - \eta_0)h_0}}{\eta_0} + \ln \left(\frac{\sqrt{h_0} - \sqrt{h_0 - \eta_0}}{\sqrt{h_0}} \right) = \frac{2}{\chi^0} \sqrt{g h_0 \frac{(g_1 - g_0)}{g_1}} t = \tau \quad (6)$$

The right hand side of (6) includes known quantities only and such could be calculated as soon as the initial condition and the time are known. We also know that the ratio $\frac{\eta_0}{h_0}$ or $\frac{\chi_0}{\chi_1} \left(\frac{\eta_0}{h_0} = \frac{\chi_0}{\chi_1} \right)$ has value 1 in the beginning, and as the liquid spreads, it tends to 0. We can calculate number of values for τ from (6), by putting different values of the ratio $\frac{\eta_0}{h_0}$ in the left hand side and plot a graph for $\frac{\eta_0}{h_0}$ against τ . This curve could be used now to calculate the value of $\frac{\eta_0}{h_0}$ or $\frac{\chi_0}{\chi_1}$ from the value of τ which could be calculated from the initial conditions. This curve is represented in Fig. 5 which shows the similarity to the motion of the spreading cloud

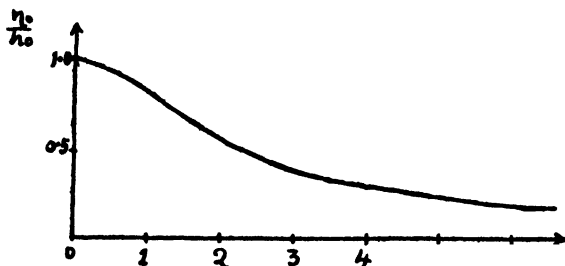


Fig. 5

(represented by the portion AB of the curve in Fig. 2).

The effect of the motion of the lighter fluid on the acceleration of the heavy fluid could be estimated by writing down the velocity potential for the lighter fluid. This motion could be represented by a number of sources and sinks and the potential at any point due to them could be calculated. The velocity potential at the surface of separation of the two fluids must be the same. The calculations are very laborious and cannot be fully given in this note. This method shows that the acceleration depends upon the initial conditions of the form of the heavy fluid. If h_0 and χ_0 represent interceptions on the axis of y and x respectively at $t=0$, then the acceleration depends upon the ratio $\frac{h_0}{\chi_0}$. As this ratio increases the acceleration decreases. The following values of the acceleration in terms of the acceleration (a) when the motion of the surrounding fluid was not considered, are given for two different values of the ratio $\frac{h_0}{\chi_0}$. The figures will show the influence on the acceleration.

$$\frac{h_0}{\chi_0} = \frac{1}{10} \quad , A = 0.88a$$

$$\frac{h_0}{\chi_0} = \frac{1}{3} \quad , A = 0.56a.$$

This partly explains why the motion calculated approximately is faster than the actual motion observed from the experiments. There is however one factor in the experiments whose influence cannot be easily estimated. This factor is the influence of the solid boundaries.

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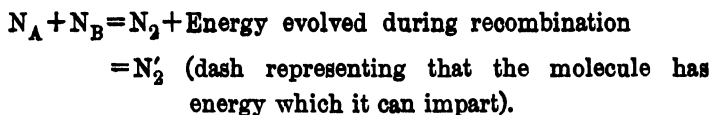
SOME THEORETICAL ASPECTS OF ACTIVE NITROGEN

By

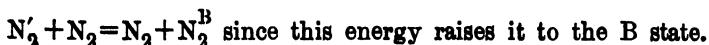
C. R. DHODAPKAR,

In my article (*The Journal of the University of Bombay*, Sept. 1935, Vol. IV, Part II, pp. 190-199) on "The present position regarding the theories about the nature of active nitrogen," it was pointed out that there are three possible views regarding the mechanism by which active nitrogen is produced and suffers decay. In one of them it is assumed that the nitrogen atoms emerge from the discharge and in a triple collision that follows combine to form a normal molecule, the energy evolved in the recombination process being utilised to excite a third partner, the normal molecule involved in the collision, from $X^1\Sigma$ state to the $B^3\pi$ state from which they emit the afterglow bands. Starting from this assertion, some mathematical deductions may be obtained—deductions which are fully borne out by some of the well-known properties of the active nitrogen.

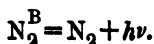
Thus in the mechanism of the afterglow bands (i) two nitrogen atoms N_A and N_B combine to form a molecule in a triple collision



(ii) the normal molecule in the triple collision absorbs all the energy evolved during the recombination process of the two nitrogen atoms; the newly formed molecule, having got rid of its energy, is in the ground state.



(iii) In the emission of the afterglow bands the molecule radiates after losing its energy thus



Let (N_A) and (N_B) represent the concentration of A and B types of the nitrogen atoms, (N_2) that of the normal molecules and (N_2^B) that of the excited molecules in the B state.

Also let K be the symbol for the velocity constant of these reactions, so that we may rewrite the above equations thus

$$K_1 \text{ for } (N_A) + (N_B) = (N'_2) \dots\dots\dots 1.$$

$$K_2 \text{ for } (N'_2) + (N_2) = (N_2^B + N_2) \dots\dots\dots 2.$$

$$K_3 \text{ for } (N_2^B) = (N_2 + h\nu) \dots\dots\dots 3.$$

In the study of the decay of the afterglow we have to consider the possibility of the energy-bearing N'_2 molecule losing its energy by collision or otherwise. Thus we have two more velocity constants:—

$$K_4 \text{ for } (N'_2) + (N_2) = 2(N_2) \dots\dots\dots 4.$$

whose energy is lost by collision.

$$K_5 \text{ for } (N'_2) = (N_2) \dots\dots\dots 5.$$

whose energy is lost by process other than collision.

The rate of production of N'_2 molecules is

$$\frac{dN'_2}{dt} = k_1(N_A)(N_B)$$

while that of disappearance is given by

$$-\frac{dN'_2}{dt} = k_2(N'_2)(N_2) + \overbrace{k_4(N'_2)(N_2) + k_5(N'_2)}^{\text{No emission}} \dots\dots\dots 6.$$

$\downarrow$
 producing N_2^B
 molecules

$\downarrow$
 Energy lost by
 collision

$\downarrow$
 Energy lost
 otherwise

When the steady state is reached, the rate of production of N'_2 will be equal to the rate of disappearance of N'_2 and therefore

$$K_1(N_A)(N_B) = K_2(N'_2)(N_2) + K_4(N'_2)(N_2) + K_5(N'_2)$$

$$\text{or } (N'_2) = \frac{K_1(N_A)(N_B)}{K_2 + (K_4 + K_5)(N_2)} \dots\dots\dots 7.$$

Equation (2) gives us the rate of production of the afterglow molecules namely excited molecules in the B state.

$$\begin{aligned} \frac{dN_2^B}{dt} &= k_2(N'_2)(N_2) \\ &= \frac{k_1 k_2 (N_A)(N_B)(N_2)}{k_2 + (k_4 + k_5)(N_2)} \dots\dots\dots 8. \end{aligned}$$

The possibility of a spontaneous reversion from N_2^B to N_2 if such reversion without collision and without emission of light

exists at all, is very small, almost negligible. Hence neglecting K_5 in equation (8), we get

$$\begin{aligned}\frac{dN_2^B}{dt} &= \frac{k_1 k_2 (N_A)(N_B)(N_2)}{(k_2 + k_4)(N_2)} \\ &= \frac{k' (N_A)(N_B)(N_2)}{(k_2 + k_4)(N_2)}\end{aligned}$$

where K' is the velocity constant for the formation of N_2^B molecules in a triple collision.

$$= \frac{k' (N_A)(N_B)}{k_2 + k_4} \quad (9)$$

It follows from this equation that the intensity of the afterglow which is proportional to the rate of disappearance of the N_2^B molecules varies as $(N_A)(N_B)$. The reaction in the afterglow is therefore bimolecular in the atoms. The rate of decay of the intensity of the afterglow, which in steady state would be equal to the rate of the production of N_2^B molecules, has been studied at different times and by different methods and is found to follow a course which is characteristic of bimolecular reactions (Phys. Zeits. 1921, 22, 97; Zeits. f. Electrochemie, 1926, 32, 536; Journal, Franklin Institute, 1926, 201, 247). This affords us with an experimental evidence regarding the reaction in the afterglow being bimolecular in the atoms.

Equation (9) further shows that the rate of production of molecules in the B state is proportional to the constant K' , the rate of recombination of atoms of A and B types in a triple collision with N_2 molecule. In a rarefied gas the chance of recombination of atoms into molecules by triple collision in which are involved two atoms and a normal molecule is rare. K' is therefore a small quantity and the concentration of N_2^B molecules which is responsible for the production of the afterglow bands will naturally form a very small proportion. Unfortunately the order of magnitude of K' —the velocity reaction of the triple collision in which are involved two atoms and a molecule—has not been ascertained so far, as the experimental material of this type is very scanty. In this connection a mention may be made of the work of Kallman and London (Zeits. Physik. Chemie, 1929, 2B, 207) although its accuracy has been questioned by O. K. Rice (Proc. Natl. Acad. Sci., 1931, 17, 34). We can however state that this mathematical deduction agrees in a qualitative way with the finding

of Lord Rayleigh (Proc. Roy. Soc. A, 1911, 85, 219). In a typical experiment which he performed, 2540 c.c. of glowing nitrogen were passed over phosphorus. The gain in weight of the latter was 15.5 milligrams. Thus the active nitrogen¹ absorbed was 12.2 c.c. It appears therefore that the percentage of nitrogen gas converted into active form is slightly less than 0.5%.

It would be a mistake to suppose that the energy of light emitted in the afterglow can be taken as being proportional to the concentration of N_2 molecules in the B state, for of the molecules in the B state an appreciable number might collide before radiating, the energy possessed being liberated in the form of heat. The number of such molecules in the B state as collide with the liberation of heat is proportional to τ , the average life-time of an excited molecule, and inversely proportional to T , the mean time between two collisions. Thus if N_2^B represents the number of molecules in the B state, only the fraction* $\left(1 - \frac{\tau}{T + \tau}\right) N_2^B$ of the molecules radiate light. To determine the number of emissions, we have to depend upon the afterglow. Since the number of molecules that emit light is less than the number of those that are actually in the B state, the number of emissions will be given by

$$\begin{aligned}
 & \left(1 - \frac{\tau}{T + \tau}\right) \frac{dN_2^B}{dt} \\
 &= \left(\frac{T}{T + \tau}\right) \frac{k_1 k_2 (N_A)(N_B)}{k_2 + k_4} \dots\dots\dots (\text{Ref. equation 9}) \\
 &= \frac{\frac{T}{\tau}}{\frac{T}{\tau} + 1} \cdot \frac{k_1 k_2 (N_A)(N_B)}{k_2 + k_4} \\
 &= \frac{\frac{T}{\tau} p}{\frac{T}{\tau} p + p} \cdot \frac{k_1 k_2 (N_A)(N_B)}{k_2 + k_4} \\
 &= \frac{\alpha}{\alpha + p} \cdot \frac{k_1 k_2 (N_A)(N_B)}{k_2 + k_4} \dots\dots\dots (10) \\
 &\text{where } \alpha = \frac{T}{\tau} p = \text{a constant } \dagger
 \end{aligned}$$

* (This follows from the fact that if τ , the average life-time = 0, all the molecules radiate light before they have any chance of collision. If $T = 0$ instead, all suffer collisions and no molecule can radiate).

† (Zeits. f. Physik, 1922, 10, 185).

It follows from equation (10) that the number of molecules that emit light is inversely proportional to the pressure. In gas at a greater pressure the time between two collisions being shortened, more molecules in the N_2^B state collide than radiate. The afterglow will get more and more quenched till at a sufficiently high pressure it gets visibly extinct. This deduction is quite in agreement with experiment where it is found that the glow becomes fainter with increased pressure. Even after the extinction of the glow there will be a certain number of molecules in the B state, that can still impart their energy to foreign matter. In other words, although the glow has disappeared so far as sense of vision is concerned, the gas is still active. This explains why the gas in the 'dark glow' condition is still able to excite the sodium doublet in sodium vapour. Further the average time between two collisions may be shortened by an increase in pressure, or the same object may be gained by an increase in temperature. Decrease in temperature, as is clear, diminishes the chances of collision and in consequence increases the average time between two collisions. Thus it is clear beyond doubt why an increase in temperature quenches the glow, and the decrease in temperature intensifies it.

If we take the second view regarding the mechanism by which nitrogen afterglow is produced, namely, that N_2^B molecules are produced by direct recombination of the nitrogen atoms (two body collisions), we shall have

$$\frac{d(N_2^B)}{dt} = k_1 (N_A)(N_B) \dots\dots\dots 1a$$

The afterglow light is generated by N_2^B molecules according to the reaction



The rate of disappearance of the (N_2^B) molecules by this reaction is

$$-\frac{d(N_2^B)}{dt} = k_2 (N_2^B) \dots\dots\dots 3a$$

A certain number of the molecules may also disappear as a result of collision with the N_2 molecules without radiation at a rate

$$-\frac{d(N_2^B)}{dt} = k_3 (N_2)(N_2^B) \dots\dots\dots 4a$$

while as before we might rule out the possibility of a spontaneous reversion from N_2^B to N_2 without collision and without emission of light.

If we suppose that the N_2^B molecules are in a steady state i.e. although the glow is decaying the rate is mainly determined by the recombination of the atoms, we shall have for the rate of disappearance of the glow

$$\begin{aligned} k_1(A)(B) &= \frac{d(N_2^B)}{dt} = -\sum \frac{d(N_2^B)}{dt} \\ &= k_2(N_2^B) + k_3(N_2)(N_2^B) \\ &= \{k_2 + k_3(N_2)\}(N_2^B) \\ \therefore (N_2^B) &= \frac{k_1(N_A)(N_B)}{k_2 + k_3(N_2)} \quad \dots \quad \dots \quad \dots \quad 5a \end{aligned}$$

From equation (3a) we have

$$\begin{aligned} -\frac{d(N_2^B)}{dt} &= k_2(N_2^B) \\ &= \frac{k_1 k_2 (N_A)(N_B)}{k_2 + k_3(N_2)} \quad \text{by substituting the} \\ &\quad \text{value of } (N_2^B) \text{ from } 5a \\ \text{or} \quad I &\propto \frac{k_1 k_2 (N_A)(N_B)}{k_2 + k_3(N_2)} \quad \dots \quad \dots \quad 6a \end{aligned}$$

where I is the intensity of the afterglow.

It follows from this equation that at a constant pressure—(N_2) constant—the intensity of the afterglow which is proportional to the rate of disappearance of the N_2^B molecules varies as $(N_A)(N_B)$. The reaction is therefore bimolecular in the atoms. The velocity constant K_1 being small in a rarefied gas, the concentration of N_2^B molecules is naturally very small.

Again since

$$\begin{aligned} I &\propto \frac{k_1 k_2 (N_A)(N_B)}{k_2 + k_3(N_2)} \\ \frac{dI}{dN_2} &\propto k_1 k_2 (N_A)(N_B) \frac{-k_3}{\{k_2 + k_3(N_2)\}^2} \end{aligned}$$

This would make I , the intensity, have a maximum value $K_1 (N_A) (N_B)$ for a given $(N_A) (N_B)$ and p small, where p being pressure of the gas is proportional to the concentration of N_2 molecules. It falls off steadily to zero as $p \rightarrow \infty$. For p large, $I \propto \frac{1}{p}$. From these results we arrive at exactly the same conclusions as are stated on page 120, and were derived by considering triple collisions.

It would be seen that in this alternative treatment, there is no need of the factor $\frac{T}{T+\tau}$ considered on page 119, equation (10), as the effect of collisions on the emission of light from N_2^B molecules has already been included explicitly in the theory.

This alternative treatment of the problem is comparatively simple, but unfortunately in the mechanism by which active nitrogen is produced and suffers decay, the recombination of free atoms into the energy-bearing molecules cannot occur in a two body collision for two reasons (a) a spectroscopic difficulty arises, in that we should expect a certain amount of continuous spectrum as a result of this recombination and (b) unless the two atoms meet in a triple collision with a third molecule which can remove the energy liberated in the union of two atoms, there is every reason to expect that the energy so liberated in the recombination process would again break asunder the newly formed molecule into atoms. Thus if the mechanism involves the union of atoms into molecules as we know it does, that recombination can take place only in triple collisions.

SUMMARY.

Some mathematical deductions have been obtained from the assumption that the energy-bearing molecules of nitrogen in $B^3\pi$ state are formed as a result of the recombination of free atoms in either two body or triple collisions. It has also been shown that the deductions so obtained agree very well with the experimental observations.

ACKNOWLEDGEMENT.

I am greatly indebted to Professor O. W. Richardson, F.R.S., for his many valuable suggestions to me in the preparation of this note.

UNIT CELL OF THE CRYSTALS OF *p*-AMINOBENZOIC ACID

By

MATA PRASAD, M. R. KAPADIA

and

V. C. THAKAR.

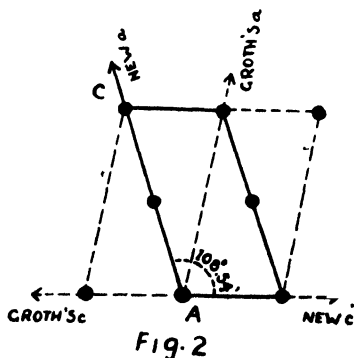
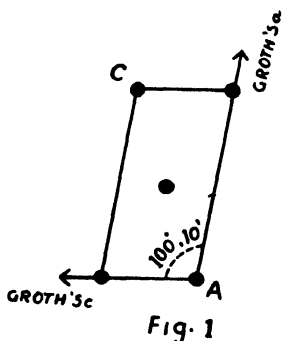
The crystals of *p*-aminobenzoic acid have been studied by the authors (J. Indian Chem. Soc., 1937, 14, 667) by means of x-rays and it was found that the dimensions of the crystallographic unit cell are

$$a = 12.26 \text{ \AA}, \quad b = 8.61 \text{ \AA}, \quad c = 6.30 \text{ \AA}, \\ \beta = 100^{\circ}10'$$

the crystals belonging to the monoclinic prismatic class.

Further it was found from several oscillation photographs taken about the crystallographic axes, that the planes (hol) are halved when $(h+1)$ is odd and that the unit cell mentioned above contains 4 molecules.

In accordance with the observed halvings there will be a molecule situated at the centre of the a - c face as shown in figure 1. This arrangement is usually disallowed in monoclinic and triclinic crystals. It is, therefore, necessary to determine a new set of axes to define the true unit cell. The relation between the crystallographic and the true unit cells is shown in figure 2.



The dimensions of the true unit cell are :—

$$a = 12.76 \text{ \AA}, \quad b = 8.61 \text{ \AA}, \quad c = 6.30 \text{ \AA}, \quad \beta = 108^\circ 54'.$$

This gives the axial ratio to be

$$1.482 : 1 : 0.732.$$

The choice of the modified cell is supported by the fact that a rotation photograph is obtained about the new 'a' axis and its observed length (AO) is the same as that calculated from the lengths of the original 'a' and 'c' axes and the original value of the angle β . The length of the new c-axis is the same as that in the original cell (*cf.* Rotation Photograph Plate III, loc. cit.). Further a smaller cell cannot be selected as such a cell will contain two molecules and will lead to an evidence for the existence of a centre of symmetry in the molecule of *p*-aminobenzoic acid which is not shown in the chemical representation of the molecules.

The planes observed in the oscillation photographs about the crystallographic *a*, *b* and *c* axes have been converted with reference to the new axes and are shown in Tables I & II.

TABLE I

Axial planes	Prism planes (hol)	Prism planes (okl)	Prism planes (hko)
001 v. s.	20 $\bar{1}$ v. s.	011 v. s.	110 m.
020 m. s.	20 $\bar{3}$ m. s.	012 s.	120 v. s.
040 m.	201 m. s.	013 v. w.	130 m. s.
200 v. s.	202 s.	021 v. s.	140 w.
400 m. s.	40 $\bar{2}$ m. s.	022 m.	210 v. s.
600 w.	40 $\bar{3}$ m. s.	031 v. s.	220 v. s.
	401 w. m.	032 m.	230 w.
	40 $\bar{2}$ s.	041 v. w.	240 w.
	60 $\bar{1}$ w. m.	042 w.	310 m. s.
	60 $\bar{2}$ v. w.		320 m. s.
			330 m.
			340 w.
			430 w. m.
			510 w. m.
			520 w.
			610 m.
			620 w.

TABLE II

General Planes

11 $\bar{1}$ v. s.	21 $\bar{1}$ s.	31 $\bar{1}$ m. s.	41 $\bar{1}$ v. s.	51 $\bar{1}$ s.	61 $\bar{1}$ m.	71 $\bar{1}$ w.
11 $\bar{2}$ m. s.	21 $\bar{2}$ m. s.	31 $\bar{2}$ m.	41 $\bar{2}$ m. s.	51 $\bar{2}$ w. m.	61 $\bar{2}$ m.	71 $\bar{2}$ w. m.
11 $\bar{3}$ w.	21 $\bar{3}$ s.	31 $\bar{3}$ s.	41 $\bar{3}$ m. s.	51 $\bar{3}$ w.	62 $\bar{1}$ m.	72 $\bar{1}$ v. s.
111 v. s.	211 v. s.	311 v. s.	411 m.	511 w.	62 $\bar{2}$ s.	72 $\bar{2}$ w. m.
112 m. s.	212 m.	312 m. s.	42 $\bar{2}$ m. s.	52 $\bar{1}$ w.		
113 m.	22 $\bar{1}$ m. s.	32 $\bar{1}$ s.	42 $\bar{3}$ w.	52 $\bar{2}$ w.		
12 $\bar{1}$ m. s.	22 $\bar{2}$ m. s.	32 $\bar{2}$ w.	421 m.	521 w.		
12 $\bar{2}$ m.	22 $\bar{3}$ w. m.	32 $\bar{3}$ w.	43 $\bar{1}$ w.	53 $\bar{1}$ m.		
121 v. s.	222 m. s.	321 s.	43 $\bar{2}$ m. s.	53 $\bar{2}$ w.		
122 v. w.	23 $\bar{1}$ m.	322 w.	431 w. m.	541 m. s.		
123 v. w.	23 $\bar{2}$ m. s.	33 $\bar{1}$ m.	44 $\bar{1}$ v. w.	54 $\bar{2}$ m.		
13 $\bar{1}$ v. w.	231 s.	33 $\bar{2}$ m. s.				
13 $\bar{2}$ m. s.	241 w. m.	331 m.				
131 m. s.		34 $\bar{1}$ m.				
132 m.		341 s.				
14 $\bar{1}$ v. w.						
141 s.						
142 m. s.						

It will be seen from these tables that the planes (hol) are halved when h is odd and the crystals belong to the same space group C^5_{2h} as obtained before. Further the number of molecules in the unit cell is 4.

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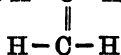
RAMAN SPECTRA OF SOME GEOMETRICAL ISOMERS*

By

B. K. VAIDYA

The geometrical isomerism exhibited by a class of organic compounds is interesting from several points of view. Unlike ordinary isomerism in space, substances showing geometrical isomerism undergo transformations, by which one form may be easily converted into the other. Thus, chemical agencies, heat treatment and light absorption under various conditions can bring about the change of one form into the other. Conclusions drawn from these transformations under different circumstances, are therefore of wide interest.

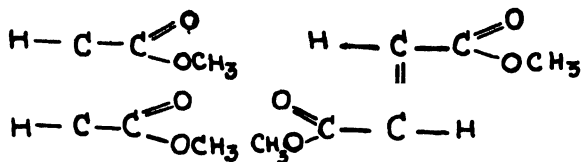
The geometric isomers containing doubly linked carbons may be looked upon as derivatives of ethylene $\text{H}-\text{C}=\text{C}-\text{H}$, obtained from



the latter by replacement of one or two hydrogen atoms connected to each of the carbon atoms. Each substance so formed is therefore capable of existence into two forms, of which generally the more labile is known as the *cis* form and the more stable as the *trans* form. Three such pairs considered in this paper are the following :—

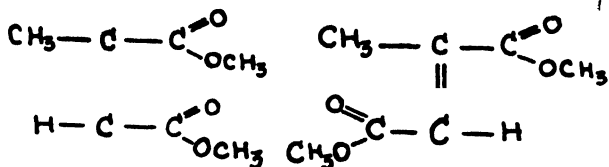


DICHLOROETHYLENE (CIS) DICHLOROETHYLENE (TRANS)



MALEIC ESTER

FUMARIC ESTER



CITRACONIC ESTER

MESACONIC ESTER

*The experimental work described in this paper was carried out at the Liverpool University in the year 1929-1930.

Since the change of one member of the pair into another in this class of substances may be fundamentally accounted for by the property of their molecules to suffer a torsion about the carbon double bond under a suitable influence, it is obvious that a study of such substances should be made by an examination of their Raman spectra, since such a study would reveal the characteristic vibrational and possibly torsional frequencies of their molecules.

Methyl esters of the two pairs maleic-fumaric and citraconic-mesaconic acids were chosen for investigation, as these with the exception of fumaric ester are obtainable in liquid form. Kohlrausch and collaborators (Sitzber. Akad. Wiss. Wien, 1931, 140, 353; Zeit. El. Chem., 1937, 43, 288) and very recently Briner, Franck and Perrottet (Helv. Chim. Act., 1939, 22, 224), have also photographed these two pairs. In the discussion of the results, best values for the Raman frequencies for each of the isomers are chosen from the above mentioned workers' as well as the author's data.

EXPERIMENTAL

The dimethyl esters of all the four acids were prepared by treating their methyl alcoholic solutions either with sulphuric or hydrochloric acid under suitable conditions. The products after necessary purification showed correct boiling points (Maleic ester b. p. 204°C , Fumaric ester solid, sublimed at 200°C , citraconic ester b. p. 210°C and mesaconic ester b. p. 203°C).

The exposure tube of 75 c.c. capacity was of the Wood type, while illumination was provided by a horizontal mercury arc. Suitable aluminium reflectors were also placed above the tube. The scattered light from the tube was focussed by means of a large condenser, on to the slit of a Hilger spectrograph of the Littrow type. This instrument gives a dispersion of $50 \text{ \AA}/\text{mm.}$ at the red end and $12 \text{ \AA}/\text{mm.}$ at the violet end of the spectrum. Because of the large dispersion and low intensity of illumination exposures of the order of 48 hours were necessary on Ilford panchromatic plates H and D 700. Comparison was made with the directly photographed mercury spectrum and the wave lengths of Raman lines were calculated by a modified form of Hartman's formula. Fig. 1 shows the mercury arc spectrum together with the Raman spectra of some of the esters investigated,

The characteristic Raman frequencies obtained in case of all the substance examined are shown below (frequencies are expressed in wave numbers cm^{-1} . while their respective intensities are given in parenthesis).

RESULTS

(1) Dimethyl maleate :—

3057(2), 2953(2), 2848(0), 2789(0), 2698(0), 2635(0),
1730(4), 1647(3), 1451(1), 1388(0), 1180(3), 1074(0),
929(1), 865(2), 598(0), 484(0), 468(1), 330(0).

(2) Dimethyl fumarate (saturated in chloroform) :—

2950(1), 1716(2), 1640(2).

The rest of the observed frequencies in this case were due to the solvent.

(3) Dimethyl citraconate :—

2961(3), 2937(3), 2911(1), 2839(0), 2755(0), 2696(0),
2624(0), 1719(3), 1645(3), 1441(2), 1374(2), 1285(1),
1256(1), 1169(2), 1086(0), 1040(0), 993(1), 928(1),
841(1), 605(0), 577(0), 470(0), 417(0), 362(1),
255(1), 217(1).

(4) Dimethyl mesaconate :—

2953(1), 2841(0), 2773(0), 2706(0), 2626(0), 1725(3),
1640(3), 1447(1), 1382(0), 1279(0), 1254(0), 1219(1),
1196(1), 1104(0), 1041(1), 997(0), 922(0), 836(1),
822(0), 762(1), 495(0), 422(0), 326(0).

DISCUSSION

In the pairs of geometrical isomers under discussion, we may assume that their structure is very similar to that of the simple ethylene molecule. To start with we may take the two forms of di-chloroethylene, the Raman spectra of which have been studied by Bonino (*Gaz. Chim. Ital.*, 1929, 59, 648), and compare their frequencies with those of the ethylene molecule which have been theoretically worked out by Mecke (*Zeit. Phys. Chem. B.*, 1932, 17 1; also see, H. Sponer 'Molekulspektren,' I, page 89, Berlin, 1935). Fig. 2 shows the various modes of oscillations of the ethylene molecule according to Mecke, together with the characteristic designation of each mode and its frequency of vibration. Out of the possible $3N - 6 = 12$ (where $N = 6$ is the number of nuclei in the molecule) frequencies those to be expected in the Raman effect

are six, while the rest are shown only in the infra red spectrum.

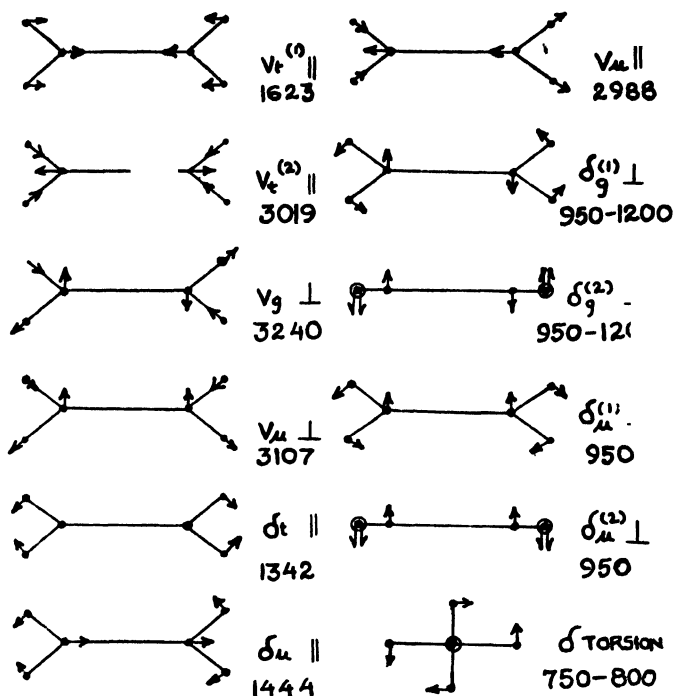


Figure 2

Vibration modes of ethylene molecule.

The torsional frequency of the molecule which has a value below 800 cm^{-1} is not observed.

In Table 1, a comparison is made of the various frequencies of the ethylene molecule with those of the two isomeric dichloroethylenes. It will be seen that all the six active Raman frequencies found in ethylene are reproduced with little variations by both the forms of dichloroethylene, although there are marked differences in intensities for the same frequencies. Thus the transverse ethylene frequency 1100 cm^{-1} appears as the frequency 1184 cm^{-1} in *cis* dichloroethylene with great intensity (5), while it fades down to a minimum of (0) in the *trans* compound. This particular mode of vibration is probably one of those responsible for changing the *cis* compound to the *trans* configuration and hence there is a very large number of molecules vibrating with this frequency in the more labile *cis* form, while their number in *trans* molecule is much reduced.

Other notable difference between the *cis* and the *trans* forms occur in the frequencies below 800 cm^{-1} . They originate in the torsional motion of the molecule, as influenced by the attractive and repulsive nature of the forces of the like and unlike groups in the *cis* and the *trans* forms respectively.

The frequency 1273 cm^{-1} in *trans* dichloroethylene is conspicuous by its absence in the *cis* molecule and therefore more difficult to explain. It usually occurs in the long chain carbon compounds and is generally ascribed to a deformation vibration of $:\text{CH}_2$ group. If its presence in *trans* dichloroethylene is not spurious, this frequency should be due to a form of vibration of $=\text{CHCl}$ group which takes place with greater facility when two like groups are furthest.

We may now consider the Raman spectra of maleic, fumaric and citraconic mesaconic esters. The vibration frequencies of these molecules are shown in Table II. The values are taken as the best representative from the present work as well as from the results of previous authors.

Here again it will be seen that all the six fundamental frequencies of the ethylene molecule are shown by both the pairs of esters. In addition due to various kinds of substituted groups in the original ethylene molecule, characteristic frequencies of various linkages in these groups make their appearance. Of these frequencies, those between the wave numbers 3000 and 2600 cm^{-1} arise out of the various modes of C-H vibration, the frequency 1724 cm^{-1} is due to $:\text{C}=\text{O}$, while frequencies round about 1273 and 1445 cm^{-1} arise from the deformations of $:\text{CH}_2$ group.

Dadiou and Kohlrausch as well as Briner, Franck and Perrottet (loc. cit.) identify the frequency 1843 cm^{-1} found by them in maleic and citraconic esters as characteristic of the *cis* form only, but the line corresponding to this frequency could not be located on author's plates.

Frequencies below 800 cm^{-1} should be ascribed to the torsional movement of the molecule about the carbon double bond as mentioned before in the case of dichloroethylene. The ester groups also possibly suffer a torque and give rise to low frequencies. Actually in each of the two pairs of isomers it is possible to classify the low frequencies into two classes, as those which belong to the torsion of the molecule as a whole and those which belong to the torsion of substituted groups in the molecule. The first type of frequencies which show marked differences in a

single pair, may be then taken as typical of the *cis* or the *trans* configuration. Such frequencies are marked in the tables with an asterisk.

TABLE I.
Raman frequencies in Dichloroethylenes.

Frequency Type	Ethylene ν in cm^{-1}	<i>cis</i> Dichloroethy- lene ν in cm^{-1}	<i>trans</i> Dichloroethy- lene ν in cm^{-1}
1 $V_g \perp$ R	3240		
2 $V_u \perp$	3107		
3 $V_t^{(2)} \parallel$ R	3019	3081 (2)	3079 (3)
4 $V_u \parallel$	2988		
5 $V_t^{(1)} \parallel$ R	1623	1588 (5)	1583 (5)
6 $\delta_u \parallel$	1444		
7 $\delta_t \parallel$ R	1342	1381 (2)	1374 (2)
8 $\delta^1_g \perp$ R	1100	1184 (5)	1273 (5) 1189 (0)
9 $\delta^2_g \perp$ R	970	882 (1)	842 (0)
10 $\delta^1_u \perp$	950		
11 $\delta^2_u \perp$	940		
12 δ (Torsion)	750-800		763* (2)
		716 (5)	717 (0)
		568* (3)	
		407* (5)	
			243* (5)
		171* (5)	

ν valence vibration; δ deformation vibration; t totally symmetric; g and u 'gerade' and 'ungerade' vibrations about the centre of symmetry.

In Tables I and II figures in bracket indicate the intensity of the lines corresponding to the respective frequencies. An asterisk mark indicates a frequency characteristic of the *cis* or the *trans* form.

TABLE II.

Raman frequencies in Esters.

Maleic ester ν in cm^{-1}	Fumaric ester ν in cm^{-1}	Citraconic ester ν in cm^{-1}	Mesaconic ester ν in cm^{-1}	Vibration group and mode
3057 (2)	3070	3045 (2)	3033 (2)	Ethylene Type 3
2953 (2)	2950 (1)	2954 (3)	2946 (3)	C - H
		2911 (1)		
2848 (0)		2848 (2)	2850 (1)	
2698 (0)		2696 (0)	2706 (0)	
2635 (0)		2624 (0)	2626 (0)	
1730 (4)	1724	1719 (3)	1725 (3)	=C : O
1647 (3)	1640 (2)	1645 (3)	1640 (3)	Ethylene Type 5
1448 (1)	1440	1441 (2)	1442 (2)	=CH ₂
1388 (0)		1374 (2)	1377 (1)	Ethylene Type 7
		1275 (1)	1273 (1)	=CH ₂
		1256 (1)	1254 (0)	
1180 (3)	1206	1193 (2)	1196 (1)	Ethylene Type 8
1074 (0)		1086 (0)	1074 (0)	=C. O
1010	1036	1040 (1)	1041 (1)	
993	997	993 (1)	997 (0)	Ethylene Type 9
929 (1)		928 (1)	922 (0)	Ethylene Type 10 and 11
864 (2)	892 (2)	891 (1)	894 (1)	
		841 (1)	836 (1)	
		772 (2)	780 (1)	
			742* (2)	Torsional vibrations of Type 12 in Ethylene together with the torsional vibrations of the substituted groups.
606	594	610 (1)	610 (2)	
		573 (2)	572 (1)	
484 (0)		470 (0)	495 (0)	
462 (1)				
		417 (0)	422 (0)	
341	331	342 (2)	331 (1)	
		295* (2)		
245		247 (1)	245 (1)	
		217 (1)	224 (1)	
		192 (2)		

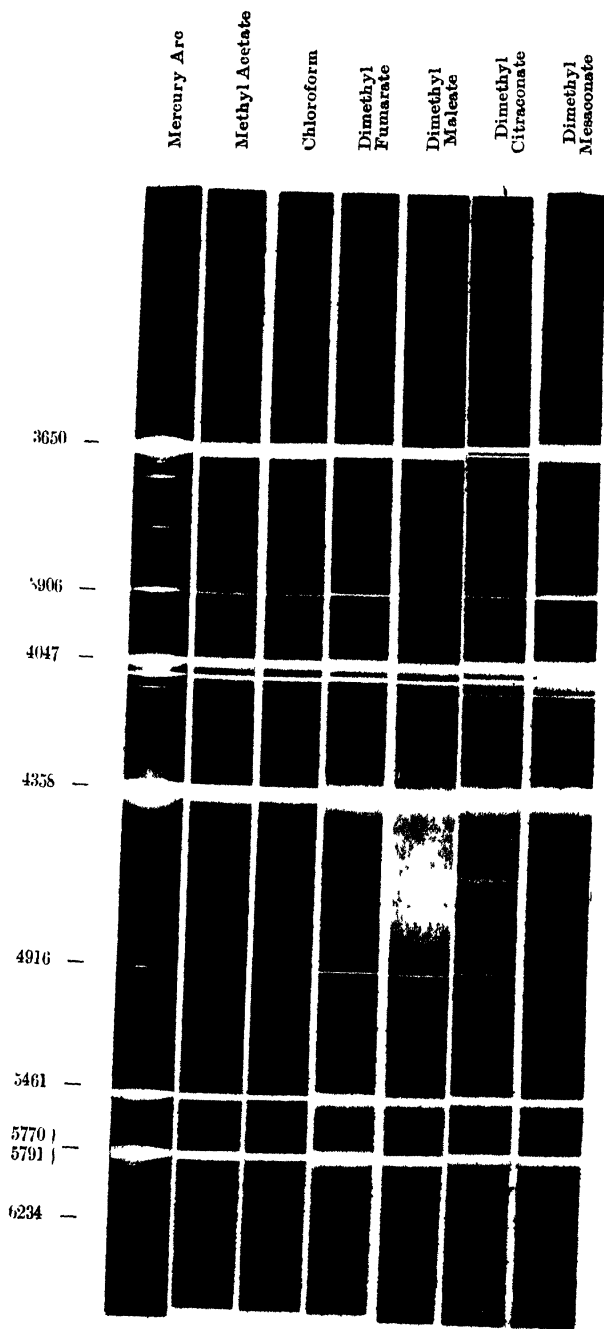


Figure 1
RAMAN SPECTRA

SUMMARY

Photographs of the Raman spectra of two pairs of geometric isomers—methyl esters of maleic-fumaric and citraconic measaconic acids have been taken on a large dispersion spectrograph of the Littrow type. The results are compared with those of the other workers on the same substances as well as with another pair of geometric isomers, namely, *cis* and *trans* dichloroethylenes.

From a consideration of the various Raman frequencies shown by the three pairs mentioned above it is shown that from a structural point of view, such types of molecules may be treated as obeying the mechanics of the simple ethylene molecule. Suggestions regarding the possible vibrational and torsional motions responsible for the labile nature of the *cis-trans* pair have been advanced.

My thanks are due to Mr. P. K. Sathe, B.E., of this Department, who prepared drawings for this paper.

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MUTUAL COAGULATION OF COLLOIDAL SOLUTIONS

PART II—INTERACTION OF PRUSSIAN BLUE AND (a) THORIUM HYDROXIDE AND (b) CERIC HYDROXIDE SOLS.

By

P. M. BARVE, V. C. VORA* AND B. N. DESAI.

In a previous paper Barve, Paranjpe and Desai [J. Bom. Univ., 1937, 6 (Part II), 50] have studied coagulation of colloidal ferric hydroxide (+vely charged) and prussian blue (-vely charged), and observed that with progress of dialysis the width of the zone of mutual coagulation first decreases and then increases, the charge on the particles of the two sols first increasing and then decreasing at the same time. In the present paper the results of similar experiments of mutual coagulation of -vely charged prussian blue and +vely charged (a) thorium hydroxide and (b) ceric hydroxide are presented. The pairs prussian blue and thorium hydroxide and prussian blue and ceric hydroxide have been selected with an idea that all the sols are acidic like prussian blue and ferric hydroxide and the peptising electrolytes oxalic acid and HCl as well as other impurities in the sols may not chemically react when the sols are mixed.

EXPERIMENTAL.

Prussian blue sol, was prepared in the same manner as before (loc. cit.). Thorium hydroxide sol was prepared in the same manner as done by Desai and Desai (Trans. Faraday Soc., 1934, 30, 265).

For the preparation of ceric hydroxide sol about 20 gm. of ceric ammonium nitrate were dissolved in distilled water and ceric hydroxide was precipitated by adding excess of ammonia. The precipitate was washed free from ammonia with hot water and suspended in one litre of distilled water. The suspension was boiled and continuously stirred and at intervals of few a minutes, 2 to 3 c.c. of 2 N.HCl were added to it. Evaporated water was replaced by addition of distilled water from time to time. After three to four hour heating, clear flourescent golden yellow ceric hydroxide sos was obtained.

Dialysis of the sols and measurements of the charge on the particles *i.e.* determination of the cataphoretic speed were carried out as before (loc. cit.).

*The experimental work has been carried out entirely by Mr. V. C. Vora under the direction of the other two authors.

The zone of coagulation was first determined roughly by finding out in each case the amounts of the two reacting sols at which turbidity first appears and then disappears as done before (loc. cit.), the total volume of the mixture being kept 10 c.c. The zone of complete coagulation was afterwards accurately determined by taking a number of mixtures in the boundary region of the zone previously roughly determined by varying the amount of the colloids by 0.05 c.c. The mixtures were then centrifuged for 3 minutes at about 2500 r.p.m. and examined for complete coagulation. When the presence of a small amount of colloid was not readily determined in the supernatant liquid by visual observation, the latter was pipetted off and treated with an excess of K_2SO_4 in the case of prussian blue and thorium hydroxide and NH_4Cl in the case of prussian blue and ceric hydroxide. The absence of any turbidity on standing was taken as an indication that no colloid was present in the supernatant liquid.

RESULTS AND DISCUSSIONS.

The results of charge measurements are given in Table I and of mutual coagulation in Tables II and III.

TABLE I.

Days of Dialysis	Cataphoretic Speed X 10^*		
	Prussian blue	Thorium hydroxide	Ceric hydroxide
0	25.6	28.9	14.3
3	29.8	34.0	—
4	—	—	18.1
7	—	—	25.2
8	36.6	38.1	—
11	—	—	33.6
12	40.7	41.3	—
15			42.9
16	45.0	42.0	—
19	—	—	34.7
20	35.6	32.4	—
23	—	—	23.6
24	31.9	27.5	—

TABLE II

Mutual coagulation of prussian blue by thorium hydroxide.

(Numbers in different columns refer to c.c. of thorium hydroxide in 10 c.c. of the mixture of thorium hydroxide and prussian blue.

A = Appearance of turbidity. Z = Zone of coagulation.

D = Disappearance of turbidity).

		Days of dialysis of prussian blue							
		0	3	8	12	16	20	24	
Days of dialysis of thorium hydroxide.		A Z D	A Z D	A Z D	A Z D	A Z D	A Z D	A Z D	
	0	1.3 <u>5.1</u> 6.4	1.1 4.8 5.9	1.1 <u>4.5</u> 5.4	1.7 3.7 5.4	1.4 <u>3.2</u> 4.6	1.2 3.1 4.3	1.0 4.1 5.1	
	3	0.9 5.1 6.0	1.2 <u>4.0</u> 5.2	1.3 4.2 5.5	1.4 3.9 5.3	1.5 3.6 5.1	1.1 3.0 4.1	1.1 4.2 5.3	
	8	1.2 4.5 5.7	1.0 3.7 4.7	1.1 <u>3.3</u> 4.4	1.3 3.0 4.3	1.7 3.3 5.0	0.9 3.8 4.7	0.8 4.4 5.2	
	12	1.0 4.1 5.1	0.8 4.2 5.0	0.9 3.8 4.7	1.8 <u>3.2</u> 5.0	1.8 2.1 3.9	1.5 3.6 5.1	0.6 4.8 5.4	
	16	0.8 5.1 5.9	0.9 4.7 5.6	0.8 4.4 5.2	1.6 3.4 5.0	8.0 <u>1.0</u> 3.0	1.0 3.7 5.6	0.7 5.1 5.8	
	20	0.7 5.3 6.0	1.1 4.9 6.1	0.7 4.7 5.4	1.2 4.1 5.3	1.7 2.8 4.5	1.6 <u>3.8</u> 5.4	1.6 4.6 6.2	
24	0.9 5.6 6.5	1.0 5.1 6.1	0.9 5.0 5.9	1.0 4.6 5.6	1.3 3.8 5.1	2.0 <u>4.2</u> 6.2	1.7 <u>4.9</u> 6.6		

TABLE III

Mutual coagulation of prussian blue by ceric hydroxide.

(Numbers in different columns refer to c.c. of ceric hydroxide in 10 c.c. of the mixture of ceric hydroxide and prussian blue.

A = Appearance of turbidity. Z = Zone of coagulation.

D = Disappearance of turbidity)

		Days of dialysis of prussian blue																				
		0			4			7			11			15			19			23		
		A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D
Days of dialysis of ceric hydroxide.	0	2.8	<u>5.7</u>	9.5	2.4	6.1	8.5	2.2	4.5	6.7	1.7	3.4	5.1	3.1	1.6	4.7	2.7	3.8	6.5	2.2	3.9	6.1
	4	2.6	6.8	9.4	3.2	<u>6.4</u>	9.6	2.9	3.4	6.3	1.3	3.8	5.1	2.7	1.8	4.5	2.4	4.2	6.6	2.0	4.3	6.3
	7	2.0	7.6	9.6	2.9	6.8	9.7	4.4	<u>2.6</u>	7.0	1.9	4.3	6.2	3.4	1.9	5.3	2.3	4.5	6.8	1.6	4.7	6.3
	11	1.7	8.1	9.8	2.3	6.3	8.6	4.1	3.3	7.4	4.0	<u>2.3</u>	6.3	3.8	1.6	5.4	2.3	4.6	6.9	1.8	5.1	6.9
	15	2.1	7.6	9.7	1.9	6.9	8.8	3.8	3.9	7.7	2.7	2.9	5.6	4.0	<u>1.2</u>	5.2	1.9	5.0	6.9	1.3	6.8	7.1
	19	1.9	7.7	9.6	1.6	7.3	8.9	3.3	4.5	7.8	2.3	3.7	6.0	3.2	2.3	5.5	1.6	<u>5.4</u>	7.0	1.1	6.5	7.6
	23	1.5	<u>8.1</u>	9.6	1.2	7.9	9.1	2.9	5.1	8.0	2.0	4.4	6.4	2.9	3.7	6.6	1.4	5.9	7.3	1.4	<u>7.3</u>	9.2

It will appear from Table I that with the progress of dialysis the cataphoretic speed *i.e.* the charge on the colloidal particles of all the three sols first increases, reaches a maximum and then decreases. These results are similar to those obtained previously by Desai and coworkers (*loc. cit.*) and can be explained in the same manner.

The changes in the range (values of Z in Tables II and III) within which mutual coagulation takes place when to one of the sols dialysed for a certain period, another sol dialysed for different periods is added are not quite regular. This is due to the fact that sols dialysed for different periods contain different amounts of impurities and will change charge on the particles differently on mixing the sole.

If one considers the range (values of Z underlined in Tables II and III) within which mutual coagulation occurs for both the sols dialysed for the same periods, it would appear that with the progress of dialysis, it *i.e.* the range first decreases, reaches a minimum value and then increases. Thus for the pairs prussian blue and thorium hydroxide and prussian blue and ceric hydroxide the range of the width of the zone of mutual coagulation is the smallest (1.0 and 1.2 units respectively) for sols dialysed for 16 and 15 days respectively. On referring to Table I it would appear that the maximum value of charge during dialysis for all these three sols has occurred at about the same time *i.e.* 15 to 16 days. The present results thus completely support the conclusions arrived at in the previous paper namely that the width of the zone of mutual coagulation is minimum when the charge on the particles is maximum. This is due to the fact that when the charge on the particles of one of the sols which is in excess is highest, the amount of the other oppositely charged colloid required to be added to coagulate it, will have to be sufficiently large so as to lower down the charge to such a value that aggregation can take place producing turbidity; similarly the disappearance of turbidity or its appearance from the other end (*i.e.*, when the second colloid is in excess and its particles have the highest charge) will occur when large amount of the coagulating colloid from that end is added. Thus the zone of precipitation will be narrowest *i.e.* the value of ' Z ' will be smallest when the particles of both the sols have greatest charge.

It should be mentioned that the lowest value of the width of the zone of mutual coagulation for the pair prussian blue and ferric hydroxide was 0.1 unit (*loc. cit.*), while in the present case it has been 1.0 and 1.2 units for the pairs prussian blue and

thorium hydroxide and prussian blue and ceric hydroxide respectively. This difference is probably due to the fact that ferric hydroxide is much less hydrated than either thorium hydroxide or ceric hydroxide. In what way, however, hydration affects the width of the zone is not quite clear.

SUMMARY AND CONCLUSIONS

Mutual coagulation of prussian blue and thorium hydroxide and prussian blue and ceric hydroxide has been studied. It is observed that as in the case of the mutual coagulation of prussian blue and ferric hydroxide previously studied in this laboratory, the width of the zone of mutual coagulation is minimum when the charge on the colloidal particles of both the sols is maximum.

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VELOCITY OF HYDROLYSIS OF SOME ALIPHATIC AND AROMATIC NITRILES

By

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I. INTRODUCTION

The hydrolysis of nitriles has been studied so far mostly with a view to the preparation of the corresponding amides or acids. A systematic study of the kinetics of their hydrolysis has not been made, although the second stage in that process, *viz.* the hydrolysis of acid amides has been studied by a number of workers. (*Cf.* Reid, *Am. Chem. J.*, 1899, *21*, 284; Crocker, *J. C. S.*, 1907, *91*, 593; Benrath, *Z. anorg. allg. Chem.*, 1926, *151*, 53; Taylor, *J. C. S.*, 1930, 2741). Recently Krieble and his co-workers (*J. Am. Chem. Soc.*, 1938, *60*, 2976; 1939, *61*, 560) have published some work on the hydrolysis of nitriles after the present investigation was practically completed. They however use much weaker solutions of the hydrolysing acids and also use no solvents.

It was therefore thought desirable to undertake a study of the hydrolysis of some representative nitriles of the aliphatic and aromatic series, especially with fairly concentrated solutions of sulphuric acids.

In the present paper are presented the results of the hydrolysis of the following nitriles:—

A. Aliphatic

1. Aceto-nitrile (B. P. 80°).
2. Propio-nitrile (B. P. 95°).
3. *n*-Butyro-nitrile (B. P. 114°).
4. *n*-Valero-nitrile (B. P. 139°).
5. *iso*-Valero-nitrile (B. P. 125°).

B. Aromatic

1. Benzo-nitrile (B. P. 189°).
2. Benzyl cyanide (B. P. 229-230°).
3. *o*-Tolu-nitrile (B. P. 199-200°).
4. *m*-Tolu-nitrile (B. P. 213°).
5. *p*-Tolu-nitrile (B. P. 214°).
6. *p*-Chlor-benzo-nitrile (M. P. 90°).
7. *p*-Brom-benzo-nitrile (M. P. 113°).

II. EXPERIMENTAL*

The nitriles used were either procured from well-known firms or prepared in the laboratory. The purification was carried out until a constant m.p. or b.p. was obtained. For each observation a quantity of nitrile equal to 1/400 mol., proportional to 25 c.c. of N/10 Sulphuric acid, was necessary and an amount equivalent to 10 such observations was weighed out. It was then dissolved in 100 c.c. of glacial acetic acid and 10 c.c. of this solution were used for each reading.

The hydrolysis was carried out in reaction tubes of capacity equal to 55-60 c.c., fitted with an air condenser about 30 cm. long and placed in a boiling water bath. After the acetic acid solution of the nitrile had attained the temperature of the water bath, 5 c.c. of sulphuric acid of known strength (the hydrolysing agent), also brought to the same temperature, were added. After the required intervals of time, *i.e.* 30, 60, 90 and 150 minutes, two of the tubes were removed, quickly cooled in running cold water and the amount of hydrolysis determined. The reaction takes place in two stages as represented below:—



*Method of estimating the decomposition products:—*The method used was that employed by Reid (*loc. cit.*) and by Taylor (*loc. cit.*), in their study of amide hydrolysis, with slight modifications so as to be applicable to nitrile-hydrolysis. The contents of the tube were transferred to a liter flask and the

*For further details, *cf.* Gharpure, M.Sc. Thesis, Bombay University, 1939.

free acid exactly neutralised by 5 N sodium hydroxide. (This amount was previously determined by titrating a mixture of 5 c.c. of the sulphuric acid used and 10 c.c. of glacial acetic acid by 5 N sodium hydroxide). 25 c.c. of magnesium sulphate solution (containing 240.0 gm. per liter) were then added. To this was added 30 c.c. of 1 N sodium hydroxide in order to form freshly precipitated magnesium hydroxide in the solution. This amount of alkali is slightly less than that required to react with the whole of the magnesium sulphate, so that an excess of the alkali is avoided, while the quantity of magnesium hydroxide formed is sufficient to decompose the whole of the ammonium salt produced in the hydrolysis of the nitrile. The contents of the flask are then diluted to about 750 c. c. and the ammonia distilled off in a Kjeldahl apparatus. The ammonia is absorbed in standard acid, the excess being titrated by standard alkali. Along with the ammonia, the undecomposed nitrile, which is volatile with steam, also distilled over, so that only the amide remained behind.

Estimation of the amide:—The contents of the flask were cooled, diluted and 20 c. c. of 5 N sodium hydroxide were added. The amide is then estimated by absorbing the ammonia given out according to the equation: $\text{RCONH}_2 + \text{NaOH} = \text{RCOONa} + \text{NH}_3$, in excess of standard acid and titrating the excess with standard alkali.

For the titrations in both the estimations we used as indicator sodium alizarine sulphonate, which was found to give very good results. For the calculation of the velocity constant, the infinity reading was obtained by boiling 10 c. c. of the acetic acid solution of the nitrile with 20 c. c. of 20 N sulphuric acid and estimating the ammonium salt formed by the usual Kjeldahl method.

III. RESULTS

A. Aromatic nitriles

The results of the velocity measurements are given in the following tables. K was calculated according to the monomolecular formula: $-K = \frac{2.3}{t} \log \frac{a}{a-x}$. The values in columns 3 and 4 are given in terms of c.c.s of N/10 H_2SO_4 , corresponding to the ammonium salt and the amide respectively.

TABLE I

Velocity of hydrolysis of Benzonitrile.

(Weight of benzonitrile for each observation = 0.2575 grm. = 25 c.c of N/10 H_2SO_4)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	30	0.14	2.15	2.39	0.003343
	60	0.57	3.91	4.48	0.003285
	90	1.20	5.21	6.41	0.003286
	150	1.95	7.79	9.74	0.003287
*Mean value of K					0.003286
20.54 N	30	0.37	3.52	3.89	0.005627
	60	0.54	6.56	7.10	0.005557
	90	0.78	9.07	9.85	0.005559
	150	1.31	12.84	14.15	0.005556
Mean value of K					0.005557
22.27 N	30	0.57	4.08	4.65	0.006847
	60	0.78	7.51	8.29	0.006779
	90	0.89	10.54	11.43	0.006782
	150	2.16	13.81	15.97	0.006779
Mean value of K					0.006780
26.208 N	30	0.88	6.94	7.82	0.01264
	60	0.99	11.86	12.85	0.01200
	90	1.31	15.21	16.52	0.01200
	150	4.07	16.78	20.85	0.01199
Mean value of K					0.01199

* In calculating the mean, the first value which is rather high is neglected.

TABLE II

Benzyl Cyanide.

(Weight taken for each observation = 0.2925 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	30	3.01	2.24	5.25	0.007843
	60	5.48	3.79	9.27	0.007723
	90	8.46	4.07	12.53	0.007718
	150	12.33	4.84	17.17	0.007729
Mean value of K					0.007725
20.54 N	30	5.46	4.32	8.78	0.01471
	60	9.53	4.36	13.89	0.01350
	90	13.21	4.43	17.64	0.01357
	150	21.53	3.47	25.00	
Mean value of K					0.01352
22.27 N	30	5.85	4.87	10.72	0.01867
	60	11.46	5.08	16.54	0.01803
	90	14.38	5.60	19.98	0.01798
	150				
Mean value of K					0.01802
26.208 N	30	15.91	4.15	20.06	0.05399
	60				
	90				
	150				

TABLE III

Ortho-tolu-nitrile

(Weight for each observation = 0.2925 gr.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	180	0.00	0.00	0.00	
	240	0.00	0.08	0.08	0.0001246
	360	0.08	0.18	0.26	
	420	0.08	0.38	0.46	
20.54 N	180	0.00	0.48	0.48	0.0001060
	240	0.18	0.78	0.96	
	360	0.28	0.98	1.26	
	420	0.38	1.08	1.46	
22.27 N	180	0.00	0.48	0.48	0.0001060
	240	0.08	0.78	0.86	
	360	0.28	1.18	1.46	
	420	0.38	1.28	1.66	
26.208 N	180	0.00	0.98	0.98	0.0001571
	240	0.18	1.08	1.26	
	360	0.38	1.28	1.66	
	420	0.48	1.48	1.96	

TABLE IV

Para-tolu-nitrile

(Weight taken for each observation = 0.2925 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	30	0.12	3.47	3.59	0.005159
	60	0.32	6.19	6.51	0.005021
	90	0.79	8.33	9.12	0.005035
	150	1.75	11.49	13.24	0.005021
Mean value of K					0.005026
20.54 N	30	0.12	4.73	4.85	0.007177
	60	0.33	8.28	8.61	0.007020
	90	1.27	10.44	11.71	0.007011
	150	2.94	13.35	16.29	0.007021
Mean value of K					0.007017
22.27 N	30	0.50	7.86	8.36	0.01355
	60	0.82	11.10	12.92	0.01211
	90	1.03	15.51	16.54	0.01203
	150	3.56	21.44	25.00	...
Mean value of K					0.01207
26.208 N	30	1.03	14.99	16.02	0.01455
	60	...	...	...	...
	90	...	...	...	...
	150	...	...	...	...

TABLE V

Meta-tolu-nitrile

(Weight taken for each observation = 0.2925 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	30	0.15	1.73	1.88	0.002614
	60	0.57	2.94	3.51	0.002519
	90	1.31	3.75	5.06	0.002515
	150	2.35	5.52	7.87	0.002516
Mean value of K					0.002517
20.54 N	30	0.36	3.51	3.87	0.005610
	60	0.78	6.30	7.08	0.005538
	90	2.03	7.80	9.83	0.005544
	150	3.92	10.19	14.11	0.005534
Mean value of K					0.005541
22.27 N	30	0.36	4.13	4.49	0.006601
	60	0.78	7.32	8.10	0.006515
	90	1.31	9.79	11.10	0.006513
	150	2.46	14.14	16.60	0.006513
Mean value of K					0.006514
26.208 N	30	0.98	9.26	10.24	0.01755
	60	2.46	13.69	16.15	0.01702
	90	3.39	16.21	19.60	0.01700
	150	...	...	...	...
Mean value of K					0.01701

TABLE VI

p-Chlor-benzo-nitrile.

(Weight taken for each observation = 0.3438 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	30	0.46	1.98	2.44	0.003412
	60	1.09	3.30	4.39	0.003319
	90	2.04	4.03	6.07	0.003322
	150	4.07	5.75	9.82	0.003321
Mean value of K					0.003320
20.54 N	30	0.78	3.61	4.39	0.006424
	60	1.51	6.44	7.95	0.006371
	90	2.97	7.92	10.89	0.006366
	150	4.75	10.65	15.40	0.006371
Mean value of K					0.006369
22.27 N	30	0.78	5.80	6.58	0.01014
	60	1.62	9.58	11.20	0.009888
	90	2.50	12.26	14.76	0.009906
	150	4.75	14.59	19.34	0.009893
Mean value of K					0.009896
26.208 N	30	2.29	11.35	13.64	0.02625
	60	2.77	16.25	19.02	0.02526
	90	—	—	—	—
	150	—	—	—	—

TABLE VII

p-Brom-benzo-nitrile

(Weight taken for each observation = 0.4550 gm.)

Conc. of H_2SO_4	Time in minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	30	0.15	1.80	1.95	0.002707
	60	0.67	3.06	3.73	0.002690
	90	1.91	3.46	5.37	0.002690
	150	3.48	4.84	8.32	0.002694
Mean value of K					0.002691
20.54 N	30	0.56	3.28	3.84	0.005550
	60	1.13	5.85	6.98	0.005446
	90	2.63	7.06	9.69	0.005441
	150	5.43	8.51	13.94	0.005439
Mean value of K					0.005442
22.27 N	30	0.77	4.70	5.47	0.008141
	60	1.39	8.13	9.52	0.007997
	90	3.07	9.74	12.81	0.007971
	150	6.04	11.40	17.44	0.007973
Mean value of K					0.007973
26.208 N	30	1.07	8.27	9.34	0.01564
	60	1.24	13.02	14.26	0.01407
	90	4.58	13.40	17.98	0.01410
	150	7.05	14.92	21.97	0.01405
Mean value of K					0.01407

The following table gives a summary of the above results on the basis of the total ammonia evolved in both the estimations and of the percentage hydrolysis with 20.54 N H_2SO_4 .

TABLE VIII

Percentage Hydrolysis

Time (min.)	Benzo- nitrile	Benzyl cyanide	o-Tolu-nitrile	m-Tolu- nitrile	p-Tolu- nitrile	p-Chlor benzo- nitrile	p-Brom benzo- nitrile
30	15.56	35.12	1.72 (180)*	15.48	19.40	17.56	15.36
60	28.40	55.56	3.84 (240)	28.32	34.44	31.80	27.92
90	39.40	70.56	5.04 (360)	39.32	46.84	43.56	39.76
150	56.60		5.84 (420)	56.44	64.06	61.60	55.76

The above results may be summarised as follows:—

1. The velocity of hydrolysis increases with an increase in the concentration of the sulphuric acid and the quantity of ammonium salt formed is always less than the quantity of amide formed.

2. Benzyl cyanide hydrolyses very much more rapidly than other aromatic cyanides and the quantity of ammonium salt formed is greater than the amide. This must be due to the fact, that the CN group is present in the side chain, so that the compound behaves like an aliphatic nitrile.

3. Ortho-tolu-nitrile is hydrolysed with great difficulty and readings had to be taken at much longer intervals (180, 240, 360 and 420 minutes) in order to get appreciable percentages of hydrolysis. Even then, however, the hydrolysis is very small, only 7.84 per cent being hydrolysed with 26.208 N sulphuric acid in 7 hours. It must therefore be concluded, that the CH_3 group in the ortho position causes steric hindrance, although it is remarkable, that a single such group should have so strong an effect.

4. In contrast to the *ortho*-compound, *para*-tolunitrile is hydrolysed with great rapidity. Thus with 22.27 N sulphuric acid, it is completely hydrolysed in less than 150 minutes and with 26.208 N acid complete hydrolysis takes place in less than an hour. The CH_3 group in the *para* position has thus an accelerating effect on the velocity of hydrolysis.

*The time is different and given in brackets.

5. The velocity of hydrolysis of *m*-tolunitrile is intermediate between the above two compounds, being slower than the para, but faster than the ortho-compound.

6. Para-chlor-benzonitrile also shows a fairly high velocity of hydrolysis, while the para-bromo compound is hydrolysed more slowly.

The order in which the velocity of hydrolysis goes on decreasing is thus as follows :—

1. benzyl cyanide ; 2. *p*-tolu-nitrile ; 3. *p*-chlor-benzonitrile ; 4. benzo-nitrile ; 5. *m*-tolu-nitrile ; 6. *p*-brom-benzonitrile ; 7. *o*-tolu-nitrile.

Further if Tables I—VII are referred to, it will be seen, that except in the case of benzyl cyanide (which resembles the aliphatic nitriles), all the other (aromatic) nitriles are hydrolysed in such a way, that a large quantity of amide is formed and a comparatively small quantity of ammonium salt. The reaction thus appears to be a consecutive reaction, where the second stage (hydrolysis of the amide) is very slow, so that a large quantity of the amide and a very small quantity of the ammonium salt results.

B. Aliphatic Nitriles

In the case of the aliphatic nitriles the hydrolysis was carried out at a temperature of 50° C. The thermostat was electrically regulated and the variation in temperature was of the order of $\pm 0.2^\circ$. The experimental procedure was otherwise identical with that of the hydrolysis of the aromatic nitriles described above.

TABLE IX

Acetonitrile

(Weight taken for each observation = 0.1025 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.84 N	30	0.55	0.45	1.00	0.001357
	60	1.19	0.65	1.84	0.001299
	90	1.89	0.90	2.79	0.001301
	150	3.81	1.13	4.44	0.001297
Mean value of K					0.001299
20.54 N	30	0.71	0.65	1.36	0.001863
	60	1.72	0.83	2.55	0.001789
	90	2.69	1.02	3.71	0.001784
	150	4.57	1.32	5.89	0.001789
Mean value of K					0.001787
22.27 N	30	0.86	0.66	1.52	0.002090
	60	1.98	0.86	2.84	0.002009
	90	3.14	1.01	4.15	0.002006
	150	5.03	1.48	6.15	0.002008
Mean value of K					0.002008
26.208 N	30	1.07	0.64	1.71	0.002354
	60	2.37	0.85	3.22	0.002292
	90	3.54	1.13	4.67	0.002296
	150	5.61	1.67	7.28	0.002291
Mean value of K					0.002293

It will be seen that here the velocity of hydrolysis increases with an increase in the acid concentration. Further, the quantity of ammonium salt formed is here greater than that of the amide, showing that the hydrolysis proceeds much more easily to the second stage. This is a characteristic of all aliphatic nitriles and of aromatic nitriles having the ON group in the side chain.

TABLE X

Propio-nitrile

(Weight taken for each observation = 0.1375 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	30	0.34	0.24	0.58	0.0007743
	60	0.74	0.39	1.13	0.0007665
	90	1.13	0.54	1.67	0.0007658
	150	2.03	0.69	2.72	0.0007665
Mean value of K					0.0007663
20.54 N	30	0.44	0.35	0.79	0.001061
	60	0.92	0.57	1.49	0.001020
	90	1.41	0.79	2.20	0.001022
	150	2.73	0.82	3.55	0.001021
Mean value of K					0.001021
22.27 N	30	0.65	0.65	1.30	0.001778
	60	1.67	0.78	2.45	0.001718
	90	2.66	0.92	3.58	0.001715
	150	4.59	1.09	5.68	0.001716
Mean value of K					0.001715
26.208 N	30	1.58	0.86	2.44	0.003412
	60	3.66	0.93	4.59	0.003369
	90	4.53	1.01	6.54	0.003368
	150	6.89	3.03	9.92	0.003367
Mean value of K					0.003368

TABLE XI

n-Butyro-nitrile

(Weight taken for each observation = 0.1725 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.34 N	30	0.06	0.05	0.11	0.0001380
	60	0.14	0.06	0.20	0.0001310
	90	0.22	0.08	0.30	0.0001310
	150	0.39	0.10	0.49	0.0001303
Mean value of K					0.0001305
20.54 N	30	0.13	0.12	0.25	0.0003297
	60	0.35	0.13	0.48	0.0003181
	90	0.56	0.15	0.71	0.0003196
	150	0.79	0.38	1.71	0.0003174
Mean value of K					0.0003184
22.27 N	30	0.38	0.20	0.58	0.0007743
	60	0.75	0.39	1.14	0.0007672
	90	1.21	0.50	1.71	0.0007669
	150	1.97	0.77	2.74	0.0007667
Mean value of K					0.0007669
26.208 N	30	0.94	0.82	1.76	0.002431
	60	2.31	1.06	3.37	0.002407
	90	3.69	1.08	4.87	0.002405
	150	5.43	1.16	7.59	0.002403
Mean value of K					0.002405

TABLE XII

n-Valero-nitrile

(Weight taken for each observation = 0.2075 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.84 N	30	0.58	0.43	1.01	0.001842
	60	1.21	0.58	1.89	0.001815
	90	2.13	0.74	2.81	0.001824
	150	3.52	0.96	4.48	0.001814
Mean value of K					0.001818
20.54 N	30	1.29	1.22	2.51	0.003527
	60	3.24	1.51	4.75	0.003502
	90	5.08	1.71	6.79	0.003510
	150	8.32	1.93	10.25	0.003513
Mean value of K					0.003508
22.27 N	30	1.39	1.39	2.78	0.003917
	60	5.01	1.59	6.60	0.005101
	90	5.94	1.46	7.40	0.003894
	150	9.56	1.49	11.05	0.003884
Mean value of K					0.003889
26.208 N	30	2.20	1.39	3.59	0.005159
	60	5.01	1.59	6.60	0.005101
	90	7.55	1.67	9.22	0.005106
	150	11.51	1.87	13.38	0.005100
Mean value of K					0.005102

TABLE XIII

iso-Valero-nitrile

(Weight taken for each observation = 0.2075 gm.)

Conc. of H_2SO_4	Time in Minutes	NH_4 Salt	Amide	Total NH_3	K
16.37 N	30	...	...	...	...
	60	0.05	0.05	0.10	0.00006515
	90	0.09	0.06	0.15	0.00006389
	150	0.14	0.10	0.24	0.00006287
20.54 N	30	0.06	0.04	0.10	0.0001334
	60	0.11	0.08	0.19	0.0001227
	90	0.18	0.10	0.28	0.0001227
	150	0.29	0.17	0.46	0.0001227
Mean value of K					0.0001227
22.27 N	30	0.40	0.36	0.76	0.001033
	60	0.83	0.67	1.50	0.001027
	90	1.53	0.69	2.22	0.001032
	150	2.69	0.89	3.58	0.001029
Mean value of K					0.001029
26.208 N	30	0.77	0.41	1.18	0.001653
	60	1.58	0.76	2.34	0.001632
	90	2.52	0.91	3.43	0.001629
	150	4.23	1.91	5.42	0.001629
Mean value of K					0.001633

The following table gives a summary of the results of the hydrolysis of the above 5 aliphatic nitriles with 20.54 N sulphuric acid.

TABLE XIV

Hydrolysis Percentage

Time in Minutes	Aceto-nitrile	Propio-nitrile	<i>n</i> -Butyro-nitrile	<i>n</i> -Valero-nitrile	<i>iso</i> -Valero-nitrile
30	5.44	3.16	1.00	10.04	0.40
60	10.20	5.96	1.92	19.00	0.76
90	14.84	8.80	2.84	27.16	1.12
150	23.56	14.20	4.68	40.75	1.84

From the above table it will be seen that the aliphatic nitriles can be arranged in the following descending order of the velocity of hydrolysis :—

1. *n*-valeronitrile; 2. acetonitrile; 3. propionitrile;
4. *n*-butyronitrile; 5. *iso*-valeronitrile.

The branched chains evidently cause some steric hindrance in the hydrolysis of the nitriles.

By reference to tables IX to XIII, it will be seen that the aliphatic amides are hydrolysed to the ammonium salts much more easily than the aromatic amides and that in the former the quantities of ammonium salt formed are consequently greater. The second stage of the hydrolysis is thus achieved more easily.

C. Temperature coefficient

In order to obtain further knowledge of the reaction, a study of the temperature coefficient for the hydrolysis of benzonitrile and *n*-valero-nitrile was undertaken. The reactions were carried out under the same conditions as before but the temperature of the bath was kept at 70°, 80° and 90° for benzonitrile and at 50°, 60° and 70° for *n*-valeronitrile. The concentration of H₂SO₄ was 26.208 N for benzo-nitrile and 16.34 N for *n*-valeronitrile. The results are given in Tables XV and XVI.

TABLE XV

Benzo-nitrile

Temperature 70°

Time in Minutes	NH ₄ Salt	Amide	Total NH ₃	Percentage hydrolysis	K
30	0.10	0.92	1.02	4.08	0.001380
60	0.15	1.76	1.91	7.64	0.001322
90	0.27	2.54	2.81	11.24	0.001324
150	0.48	4.02	4.50	18.00	0.001320
Mean value of K					0.001322

Temperature 80°

30	0.22	2.29	2.51	10.04	0.003535
60	0.39	4.25	4.64	18.56	0.003415
90	0.60	6.05	6.66	26.64	0.003412
150	0.98	9.06	10.04	40.16	0.003417
Mean value of K					0.003415

Temperature 90°

30	0.78	6.07	6.85	27.40	0.01065
60	0.88	10.42	11.30	44.12	0.01001
90	1.11	13.93	14.84	59.36	0.009993
150	3.87	15.62	19.49	77.96	0.01007
Mean value of K					0.01000

$$\text{Temperature coefficient} = \frac{K_{80^\circ}}{K_{70^\circ}} = 2.58; \frac{K_{90^\circ}}{K_{80^\circ}} = 2.9.$$

TABLE XVI

n-Valero-nitrile*Temperature 50°*

Time in Minutes	NH ₄ Salt	Amide	Total NH ₃	Percentage Hydrolysis	K
30	0.58	0.43	1.01	4.04	0.001342
60	1.21	0.58	1.89	7.56	0.001315
90	2.30	0.74	2.81	11.24	0.001324
150	3.52	0.96	4.48	17.92	0.001314
Mean value of K					0.001318

Temperature 60°

30	1.77	0.65	2.42	9.68	0.003388
60	3.42	1.07	4.49	17.96	0.003293
90	4.89	1.53	6.42	25.68	0.003295
150	7.85	1.91	9.76	39.04	0.003296
Mean value of K					0.003295

Temperature 70°

30	4.47	1.35	5.82	23.28	0.008303
60	7.95	1.81	9.76	39.04	0.008239
90	11.12	1.98	13.10	52.03	0.008239
150					
Mean value of K					0.008239

$$\frac{K\ 70^\circ}{K\ 60^\circ} = 2.04; \frac{K\ 60^\circ}{K\ 50^\circ} = 2.5.$$

Here also we have to do with a simultaneous reaction, where the amide is much more easily hydrolysed, with the result that the quantity of ammonium salt is greater. Krieble, and Noll (loc. cit.) in a paper published after the completion of the present investigation, come to slightly different conclusions, though even they find that the branched chains offer some resistance to the hydrolysis of the aliphatic nitriles. Further they use for hydrolysis acids of lower concentration (1.0 N to 8.0 N) and no solvent. Our results are therefore not strictly comparable.

The results obtained may be summarised as follows:—

1. In the case of the aromatic nitriles, the hydrolysis proceeds easily upto the amide stage, so that the quantity of ammonium salt formed is always small. The CH_3 group in the ortho position offers considerable steric hindrance; para-tolunitrile is hydrolysed more rapidly than meta-tolunitrile. Similarly *p*-chlorbenzonitrile is hydrolysed more rapidly than *p*-brombenzonitrile.
2. In the case of the aliphatic nitriles, which also include benzyl cyanide, the second stage of hydrolysis appears to be more easily achieved than in the case of the aromatic nitriles, with the result, that the quantity of ammonium salt formed is greater than that of the amide.

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KINETICS OF REACTIONS IN HETEROGENEOUS SYSTEMS.—PART IV—HYDROLYSIS OF BENZYL ACETATE, BUTYL ACETATE AND ISO-AMYL ACETATE BY HYDROCHLORIC ACID

By

DINAKAR KARVÉ AND V. L. MEHENDALE.

I. INTRODUCTION.

In continuation of previous work (Parts I & II, Karve and Dole, *J. Ind. Chem. Soc.*, 1935, 12, 719, 733 ; Part III, *Jour. Univ. Bom.*, 1938, 7, Part 3) the velocity of hydrolysis of benzyl acetate, butyl acetate and iso-amyl acetate dissolved in non-aqueous solvents with aqueous hydrochloric acid was determined.

It has already been shown in the previous work, that the reactions which are ordinarily considered as heterogeneous liquid reactions may be roughly divided into two classes: those that are homo-heterogeneous and those that are purely heterogeneous. To the first class belong those reactions where the reactants do dissolve in each other to a certain extent, so that the reaction takes place at the surface of contact of the two liquid layers, as also in the interior of the liquids. The total chemical change is therefore the sum of the heterogeneous and the homogeneous reactions and their respective magnitudes would depend, among other factors, on the mutual solubility. To the second class of reactions belong those reactions, where there is no mutual solubility and the reaction therefore takes place solely at the surface of contact.

The present investigation deals with the study of the both these types of reaction. In the case of benzyl acetate, not only is the ester practically insoluble in water, but the benzyl alcohol liberated being also insoluble in water, the reaction is a purely heterogeneous one.

The hydrolysis of butyl and iso-amyl acetates on the other hand represents the first class of heterogeneous reactions, *viz.* homo-heterogeneous reactions. Although the acetates themselves are only very slightly soluble in the aqueous layer, the butyl and iso-amyl alcohols liberated are appreciably so, and they in their turn dissolve some of the ester. This is then homogeneously hydrolysed and the total chemical change is therefore the sum of the two reactions: the one taking place at the surface of contact and the other in the interior of the aqueous phase. Goldschmidt and Messerschmidt (*Zeit. physik. chem.*, 1899, *31*, 255) have studied the reaction of ethyl acetate dissolved in benzene with aqueous hydrochloric acid and worked out a formula on the basis of the assumption, which is not entirely correct, that the reaction takes place only in the interior of the aqueous phase, which they assume to remain saturated all the time. They however neglected the reaction taking place at the surface of contact altogether.

II. EXPERIMENTAL.*

The reactants were mixed in 250 c.c. glass stoppered bottles and fixed in a horizontal position to the platform of a cradle-type shaking machine, which was given a definite number of to-and-fro shakes per minute. The machine was kept in a large air-thermostat, the temperature of which was electrically regulated and kept at $30^{\circ} \pm 0.1^{\circ}$. The details regarding the construction of this air-thermostat are given by Dole. (Ph.D. thesis, University of Bombay, 1937). The speed of the motor, which drove the shaking machine, was kept constant and measured by means of a stroboscopic disc attached to the pulley.

50 c.c. of the aqueous hydrochloric acid were first placed in each of the bottles and kept at 30° . After the bottles had attained this temperature, 20 c.c. of the 0.1 molar ester solution in xylene, (also kept at 30°), were added and the bottles were then shaken on the machine. After the necessary time interval one of the bottles was removed and the contents poured into a separating funnel. The aqueous layer was drawn off and titrated with standard alkali.

For calculation of the velocity constant the monomolecular formula was used, the value of "a" being determined by complete hydrolysis of the ester in the homogeneous system.

*For further details, see Mehendale, M.Sc. Thesis, Bombay Univ., 1938.

III. RESULTS

The effect of a change in the different factors governing the reaction was studied in detail.

1. The effect of the to-and-fro movement of the bottles is to mix the reactants thoroughly and although previous workers have either used stirring or other types of agitation the results obtained by us are very nearly the same. We find that the amount of reaction goes on increasing with the speed of shaking, though there is no strict proportionality between the two.

TABLE I.

Hydrolysis of benzyl acetate by 1.0 N Hydrochloric acid at 30°.

R.P.M.	Percentage hydrolysed in 1 hour.
88.4	8.55
94.5	9.76
99.0	10.98
112.0	12.20
116.6	20.76
122.6	24.42

With butyl and iso-amyl acetates also the results were similar

2. Temperature.

A. Benzyl Acetate.

As it was thought that the temperature coefficient would give an idea as regards the nature of the reaction, the hydrolysis was determined at 26°, 28°, 30°, 32°, 34° and 36°. Each time 50 c.c. of 1 N hydrochloric acid were taken with 20 c.c. of 0.1 molar solution of benzyl acetate. The value of "a" by infinity reading was 20.00. "x" is expressed in terms of c.c.s. of N/10 acid.

TABLE II

Temp.	28°		28°		30°		32°		34°		36°	
Time in hours	x	k	x	k	x	k	x	k	x	k	x	k
1	2.021,	0.0451	2.475	0.0578	0.2441	0.0568	3.025	0.0713	3.85	0.0928	3.85	0.0928
2	3.838	0.0463	4.675	0.0578	4.640	0.0538	5.575	0.0725	7.15	0.0960	7.15	0.0960
3	5.254	0.0444	6.325	0.0545	6.390	0.0547	8.250	0.0761	9.90	0.0979	9.90	0.0979
4	6.568	0.0432	7.700	0.0528	8.050	0.0537	10.175	0.0771	12.37	0.1046	12.37	0.1048
5	7.275	0.0392	8.800	0.0503	9.520	0.0501	11.825	0.0777	14.30	0.1090	14.57	0.1133
6	8.79	0.0419	9.900	0.0474	10.740	0.0509	13.200	0.0749	15.95	0.1102	16.50	0.1211
Mean k		0.0433		0.0534		0.0551		0.0749		0.1017		0.1039

Previous workers (*cf.* Kohlrausch, *Zeit. Elektrochem.*, 190, 8, 14, 129) have drawn the attention to the importance of the temperature coefficient in the case of heterogeneous reactions. In certain reactions of this type, the chemical process is slow, while the diffusion of the products of reaction into the interior of the reactants is a very fast reaction. The former would then determine the effective rate of reaction. The temperature coefficient of such a reaction would be equal to about 2.5, which is the usual coefficient for chemical reactions. The value of the temperature coefficient for diffusion of liquids has generally a much lower value, between 1.0 and 1.5. If therefore in a particular heterogeneous reaction the diffusion process is slow and determines the net velocity of the chemical change, one would expect values of 1 or 1.5 for the temperature coefficient.

From the above table it will be seen that :

$K_{36^{\circ}/K_{26^{\circ}}} = 2.404$ and it appears that the chemical process mainly determines the rate of this reaction and not the diffusion process.

B. Butyl and iso-amyl acetates.

An attempt was made to study the temperature coefficient of this reaction also. It was however not possible to get even approximately constant values for the velocity constant. This is due to the fact that although the amount of reaction at the surface of contact depends upon the concentrations of the layers, the increasing amount of the ester dissolving in the aqueous phase would increase the total percentage of the ester hydrolysed. The following table illustrates this fact clearly :—

TABLE III

Hydrolysis of 0.1 molar butyl acetate in xylene (20 c.c.) by 1.0 N aqueous hydrochloric acid (50c.c.) at 30°.

26° c.			36° c.	
Time in hours	%hydrolysed	K	%hydrolysed	K
1	12.63	0.0583	33.81	0.1757
2	18.95	0.0456	53.40	0.1648
3	25.26	0.0421	69.65	0.1740
4	31.58	0.0412	79.95	0.1744
5	37.89	0.0481	86.61	0.1746
6	41.05	0.0888	86.61	0.1455

However, even in the case of this reaction, the approximate rise in the value of K for a rise of 10° is over 3 times, so that the chemical change and not the velocity of diffusion is to be considered as the process determining the velocity of the reaction.

3. A. Benzyl acetate :

When the total volume of hydrochloric acid used in the hydrolysis was varied, it was seen that the value of the percentage hydrolysis and of the velocity constant increased upto a certain limit and then went down. This must be due to the fact, that after a certain limit the increasing volume of the acid diminished the empty space in the bottle and reduced the effective mixing up of the two layers.

TABLE IV.

Hydrolysis of benzyl acetate with different volumes of 1.0 N hydrochloric acid. (Other factors same as before).

Volume of HCl	50c.c.	100-c.c.	150 c.c.	200 c.c.
mean value of K	0.0551	0.0856	0.0806	0.0780

The same kind of results were also obtained with benzyl propionate.

B. Butyl and iso-amyl acetates :

For an increase in the volume of aqueous hydrochloric acid, the results are somewhat different from those in the hydrolysis of benzyl acetate. The velocity increases rapidly upto a maximum and then increases very slowly, showing that the efficacy of shaking is reduced if the volume of liquids in the shaking vessels goes beyond a certain maximum. This naturally reduces the heterogeneous part of the reaction. However, the homogeneous part of the reaction shows a continuous increase owing to the increasing solubility of the ester in the aqueous layer, which in turn is due to the increasing concentration of the alcohol. The following table illustrates these conclusions :—

TABLE V

Hydrolysis of butyl acetate with varying volumes of HCl.
(Concentrations, temperature, etc. same as before.)

Time in hours	50 c.c. K	100 c.c. K	150 c.c. K	200 c.c. HCl K
1	0.0570	0.0877	0.0877	0.0921
2	0.0564	0.0790	0.0984	0.0984
3	0.0502	0.0659	0.0969	0.0969
4	0.0471	0.0605	0.0865	0.0865
5	0.0467	0.0581	0.0818	0.0818
6	0.0467	0.0576	0.0805	0.0805

The results with iso-amyl acetate were analogous.

4. Concentration of acid.

A. Benzyl Acetate.

In order to ascertain the effect of a change in the concentration of the acid, 0.5, 1.0, 1.5, 2.0 and 2.5 N hydrochloric acid was used with xylene solutions of benzyl acetate and benzyl propionate. The quantities and concentrations of the esters, temperature, etc. were as in previous experiments.

TABLE VI

Concentration of HCl	Benzyl acetate					Benzyl propionate				
	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
Mean value of K	0.0369	0.0533	0.0652	0.0694	0.0785	0.0369	0.0562	0.0669	0.0723	0.0763

It will be seen that there is a regular increase in the percentage hydrolysis with an increase in the concentration of the acid.

B. Butyl and iso-amyl acetates.

As regards the effect of acid concentration on the velocity of reaction, the results are very similar to those obtained with benzyl acetate. Only, on account of the greater proportion of the homogeneous reaction with higher concentrations of HCl, the values of K varied considerably with time. Further, it was also seen, that because of the lower solubility of iso-amyl alcohol (2.7 gm. in 100 c.c. of water as compared with 8.4 gr. in 100 c.c. water in the case of butyl alcohol), the proportion of the homogeneous reaction with iso-amyl acetate was smaller and so also the variation in the values of K.

5. Influence of solvents.

A. Benzyl Acetate.

Although different solvents influence the velocity of the reaction, it was not possible to find out any definite relationship between any one physical property and the increase or decrease in the velocity constant. Among the factors which would be of importance in this connection would be, dielectric constant, density, interfacial tension with water, mutual solubility and so on. The following table gives the value of the velocity constant with 0.1 molar ester solutions in different solvents with 1.0 N aqueous hydrochloric acid. Temperature and all other factors were the same as in previous experiments.

TABLE VII

Solvent	Petrol (95-100°)	Benzene	Toluene	Xylene	Mono-chlor-benzene
Mean value of K	0.0643	0.0789	0.0679	0.0533	0.0549

It will be seen, that the solvents can be arranged in the following order of falling velocity constants: benzene, toluene, petrol, mono-chlor-benzene and xylene.

B. Butyl and iso-amyl acetates.

The solvent in which the ester is dissolved appears to influence the homo-heterogeneous reactions in the same way as the purely heterogeneous ones.

The following table gives the results obtained for the hydrolysis of 0.1 N molar solutions of butyl acetate in the solvent named with 1.0 N HCl, the volumes, temperature etc. being the same as before.

TABLE VIII

Value of K

Time in hours	Petrol (95-100°)	Benzene	Toluene	Xylene	Mono-chlor-benzene.
1	0.0587	0.0846	0.0548	0.0570	0.0431
2	0.0596	0.0783	0.0589	0.0564	0.0389
3	0.0631	0.0877	0.0509	0.0502	0.0373
4	0.0633	0.0881	0.0477	0.0471	0.0372
5	0.0650	0.0916	0.0459	0.0467	0.0362
6	0.0651	0.0954	0.0466	0.0467	0.0374

The extent of the reaction is highest in benzene and goes on diminishing with petrol-toluene-xylene-mono-chlor-benzene.

6. An attempt was made to find out the extent of the homogeneous reaction by taking a solution of 1. N hydrochloric acid and saturating it with butyl alcohol, shaking this with butyl acetate for a short time and separating the undissolved butyl acetate. The solution was then kept at 30° and the velocity of hydrolysis of the dissolved butyl acetate was determined by titrating a known volume from time to time. However, it was found that here also the values of K, calculated according to the monomolecular formula, were not constant, but increased continuously. This may probably be due to the continuous increase in the H-ion concentration caused by the liberation of acetic acid and the consequent acceleration of the reaction.

It will be seen, that the above investigation throws a considerable light on the hydrolysis of benzyl acetate by aqueous hydrochloric acid in the heterogeneous system. There is generally a small gradual increase in the value of K as the reaction proceeds, and it can be accounted for by the catalytic influence of the acetic acid liberated in the hydrolysis. This increases the H-ion concentration of the aqueous layer and raises the rate of hydrolysis. This increase is however very small under the experimental conditions and the rise in the value of K is not very much. The reaction is a purely heterogeneous reaction taking place at the surface of contact and the chemical change is slower than the process of diffusion.

In the case of the homo-heterogeneous reactions, conditions are slightly more complicated owing to the continuous increase in the velocity of the homogeneous part. Otherwise, in certain respects the hydrolysis of butyl and iso-amyl acetates is similar to that of benzyl acetate.

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INTERACTION OF SULPHURYL CHLORIDE WITH ARYLAMIDES OF AROMATIC ACIDS, PART III

By

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It has been observed by the authors in part I (J. Ind. Chem. Soc., 1938, 15, 649) that the basic part of the molecule containing two aromatic nuclei is deactivated by the introduction of electron accepting group like NO_2 in it, as is shown by the non-formation of the chloro derivative in the case of benz-*p*-and-*m*-nitranilides and benz-*p*-nitro-toluidide.

In order to study the effect of the introduction of a similar nitro group in the acidic part of the molecule, anilide and *o*-and-*p*-toluidides of *m*-and-*p*-nitrobenzoic acids were worked out. It was observed that the molecule was so much deactivated that the reaction in some cases could be brought about by boiling the reacting substances without any solvent. Even under these drastic experimental conditions only monochloro derivatives with chlorine in the basic part of the molecule could be obtained, even with large excess of sulphuryl chloride.

The constitution of the products was proved by synthesis or hydrolysis.

EXPERIMENTAL

m-Nitrobenz-*p*-chloranilide :—*m*-Nitrobenzanilide (3g.) and sulphuryl chloride (5g.) were mixed and boiled under reflux for about four hours, it being protected from moisture. The solid obtained was washed with dry petroleum ether until free from sulphuryl chloride. It was soluble in benzene, alcohol and acetic acid. It crystallised from alcohol in needles, m.p. 175° . (Found : Cl, 12.6 ; $\text{C}_{12}\text{H}_9\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 12.8 per cent.)

The constitution of the product was proved by its synthesis from *p*-chloraniline and *m*-nitrobenzoyl chloride in presence of sodium hydroxide, when the above compound showed no lowering in mixed melting point.

m-Nitrobenz-*o*-toluidide :—It was prepared from *o*-toluidine and *m*-nitrobenzoyl chloride by Schotten Baumann method and crystallised from glacial acetic acid in needles, m.p. 154° . (Found : N, 10.7 ; $\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}_2$ requires N, 10.9 per cent),

m-Nitrobenz-5-chlor-o-toluidide ($\text{CH}_3=1$). It was prepared in the same way as *m*-nitrobenz-p-chloranilide. It crystallised from alcohol in needles, m.p. 183° . (Found:—Cl, 12.0; $\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 12.2 per cent.)

The compound (lg.) was mixed with 20 c.c. of 10 percent solution of caustic potash in 50 per cent alcohol and heated in a sealed tube at 170° for six hours. The mixture was then extracted with ether and the liquid residue obtained after the removal of ether was heated with acetic anhydride, when a solid acetyl derivative was obtained. It crystallised from acetic acid in needles, m.p. 138° . It showed no lowering in melting point when mixed with an authentic specimen of acet-5-chlor-o-toluidide ($\text{OH}_3=1$) which proved that the liquid was 5-chlor-o-toluidine.

The acid obtained from the alkaline solution was proved to be *m*-nitrobenzoic acid by mixed melting point.

m-Nitrobenz-3-chlor-p-toluidide ($\text{CH}_3=1$):—It was prepared in the same way as the o-toluidide derivative and showed similar solubility. It crystallised from alcohol in pale yellow needles, m.p. 173° . (Found: Cl, 12.4; $\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 12.2 per cent.)

The compound was hydrolysed in the same way as the ortho derivative and the chloroamine obtained was identified through its acetyl derivative by mixed melting point with an authentic specimen of acet-3-chlor-p-toluidide ($\text{CH}_3=1$). The acid was found to be *m*-nitrobenzoic acid by mixed melting point.

p-Nitrobenz-p-chloranilide:—It was prepared in the same way as *m*-nitrobenz-p-chloranilide. It crystallised from alcohol in long yellow needles, m.p. 219° . (Found: Cl, 12.6; $\text{C}_{13}\text{H}_9\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 12.8 per cent.)

Constitution of the compound was proved by its synthesis from *p*-chloraniline and *p*-nitrobenzoyl chloride in presence of caustic soda, when no lowering in melting point was observed.

Hydrolysis of *p*-nitrobenz-p-chloranilide with alcoholic caustic potash under pressure as in the case of *m*-nitro-5-chlor-o-toluidide gave *p*-chloraniline which was identified through its acetyl derivative and the acid was found to be *p*-nitrobenzoic acid.

p-Nitrobenz-5-chlor-o-toluidide ($\text{CH}_3=1$):—It was prepared in the same way as *m*-nitrobenz-p-chloranilide. It crystallised from alcohol in needles, m.p. 210° . (Found: Cl, 12.1; $\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 12.2 per cent.)

This compound was hydrolysed by heating with alcoholic caustic potash as in the case of m-nitrobenz-5-chlor-o-toluidide and the amine obtained was identified through its acetyl derivative by mixed melting point.

The acid obtained was found to be p-nitrobenzoic acid by mixed melting point.

p-Nitrobenz-3-chlor-*p*-toluidide ($\text{CH}_3 = 1$):—It was prepared in the same way as m-nitrobenz-*p*-chloranilide. It crystallised from alcohol in long yellowish needles, m. p. 158° . (Found: Cl, 12.2; $\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 12.2 per cent).

The compound was hydrolysed by the same method followed for other compounds. The chloramine obtained was identified through its acetyl derivative by mixed melting point.

The acid obtained was found to be p-nitrobenzoic acid from its mixed melting point.

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A NEW SYNTHESIS OF 3-AMINOCOUMARIN

By

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Erlenmeyer, jun. and Bade have stated [1] that salicylaldehyde does not condense with glycine to give an α -amino- β -hydroxy acid in the way in which other aldehydes condense with α -amino acids by the method now associated with Erlenmeyer's name. Vanillin also was said to undergo no such condensation.

Later on [1912] Linch prepared 3-amino-coumarin by condensing salicylaldehyde with glycine in the presence of sodium acetate and acetic anhydride [2]. He was able to obtain in this way 3-acetylaminocoumarin, and, from this by hydrolysis, 3-amino-coumarin. But he found a very poor yield of the former: he states that many experiments under varying conditions were tried, but the highest yield of the 3-acetylaminocoumarin was only 25—30 per cent, which would be further reduced on hydrolysing it to the aminocoumarin. He had, therefore, to follow a roundabout method of condensing salicylaldehyde with ethyl acetoacetate [Knoevenagel, 3], to change the 3-acetylcoumarin so obtained to its oxime, which, undergoing the Beckmann transformation, gave 3-acetylaminocoumarin. This last, on careful hydrolysis, gave the base as usual. The exact yield calculated on salicylaldehyde is not stated by Linch, who, however, says the method is advantageous [loc. cit.].

Our experience of the increased yields of purer products when pyridine traces took the place of the Perkin's reagents in condensations of aldehydes [4], suggested the possibility of a straightforward condensation between salicylaldehyde and glycine in the presence of a trace of pyridine, and the experiment has succeeded beyond our expectation.

Linch's work using the Perkin reagents was first repeated, and the condensation, conducted at 120° for six hours, yielded 25 per cent of the theoretical yield of 3-acetylaminocoumarin. On hydrolysis it yielded the 3-aminocoumarin, which agreed well in properties with that described by Linch.

Salicylaldehyde, glycine and pyridine [1: 1: 0.15 mol.] were then heated at 120° for six hours, and the viscous mass on treatment with alcohol and water gave 3-aminocoumarin, melting at 130° ; a mixed melting-point with the authentic specimen previously referred to showed no depression. The yield was 50 per cent of the theory.

Further experiments to improve the yield, if possible, indicated that the optimum temperature was slightly higher, $130-140^{\circ}$, beyond which, however, a dark brown colour developed. In every case some amount of glycine remained unaffected. The highest yields of about 81 per cent were obtained when the molecular ratio of salicylaldehyde to glycine was raised to 1.5: 1.0 from 1: 1.

Thus salicylaldehyde 3 g., glycine 1.25 g. and pyridine 0.1 c.c. [molecular ratio 1.5: 1.0: 0.08] were heated together in an oil-bath at $130-140^{\circ}$ for five hours. The reaction-product was extracted in the flask several times with alcohol, which did not dissolve glycine. After filtering off the glycine, the dark red alcoholic extract was warmed and the excess of alcohol removed. To the cooled residue water was carefully added when the 3-aminocoumarin was precipitated as a yellow amorphous powder. It was filtered, washed with water, and then ground up with an excess of cold water. The crude aminocoumarin was further purified by recrystallisation from alcohol and water. It weighed 2.1 g. (81%).

When more than 1.5 mol. of the aldehyde was taken, *e.g.* 2 mol., the yield remained the same, a little glycine still remaining unacted upon at the end. Longer heating also did not help.

Salicylaldehyde and glycine, when heated alone, without pyridine, under the same conditions, also underwent the same condensation, but the yield of the aminocoumarin was only 23 per cent on the glycine taken, or 50 per cent on the glycine actually used up. [The molecular ratio was 1: 1.]

Vanillin appears to undergo condensation with glycine in the same way, but the product became dark and tarry as soon as it was taken out, and is under investigation.

SUMMARY

Salicylaldehyde and glycine undergo condensation when heated together at $130-140^{\circ}$, giving 3-aminocoumarin. By using

pyridine, the yield is raised up to about 81 per cent. This is so far the best method of preparing the compound.

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THE STERIC EFFECT OF THE NITRO-GROUP ON THE ORIENTATION OF A THIRD SUBSTITUENT IN META- NITRO-PHENOL

By

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The introduction of a third substituent into the nucleus of a substance like *m*-nitro-phenol is of great interest from several points of view. According to the common experience (Crum-Brown-Gibson Rule) the nitro-group is 'meta'-orienting whereas the phenolic hydroxyl group is 'ortho-para' orienting. In ortho- or para-nitrophenol, an 'ortho' or 'para' position to the hydroxyl group turns out to be 'meta' position to the nitro-group present. In these compounds, therefore, the orienting influence of each of these groups acts in a harmonious co-operation with that of other; whereas in meta-nitro-phenol the orienting influences of the two groups are incompatible with each other. The actual position therefore taken up by a new entering group cannot be predicted with any degree of certainty. The orienting influence of one of the groups may be more predominating over that of the other; the nature of the entering group may also considerably influence and determine the actual position taken up by the third substituent; the molecular volumes of the incoming as well as the existing groups may also have a considerable bearing on the position taken up by the new substituent; all these factors may be interdependent and as a result a mixture of isomerides may be formed. The above considerations bring out clearly the complicated nature of the problem. Before one could completely solve the problem of Aromatic substitution in all its aspects, it is necessary to accumulate exact and quantitative data about the formation and yields of isomeric compounds in a number of typical cases of aromatic substitutions. The present work is an attempt in this direction in the case of *m*-nitro-phenol. With the object of bringing out clearly the influence of as many factors as possible, three different re-acting groups:—(1) Oxy-methyl ($-\text{CH}_2\text{OH}$); (2) Aldehydo ($-\text{CHO}$) and (3) Acetoxy-mercury ($-\text{Hg}-\text{O}-\text{CO}-\text{CH}_3$) were

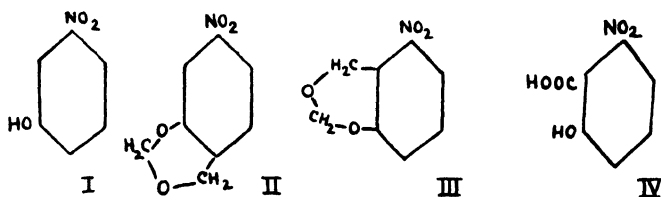
attempted to be introduced into the nucleus of m-nitro-phenol, by reaction with formaldehyde, chloroform and mercuric acetate respectively.

It is clear in the experimental part of the work from the respective yields of the isolated products and recoveries of the unchanged material that, as was expected, the reaction takes more than one course.

REACTION WITH FORMALDEHYDE

Formaldehyde has long been known to condense (Manasse Bar., 27, 2411) with phenolic compounds either in dilute caustic alkali solutions (Lederer, J. Pr. Chem. (2), 50, 225) or in acid solutions (Stoermer, Ber. 34, 2459).

The compound that we were able to isolate fairly easily from the condensation of m-nitro-phenol (I) with a slight excess of formaldehyde was a neutral body, m.p. 77° c, incapable of yielding an acetyl-derivative and from its analysis and molecular weight, had to be given the structure of a methylene ether of a nitro-hydroxy-Benzyl alcohol (II or III).



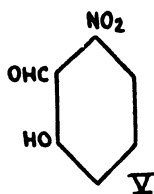
The methylene ether structure of this compound was confirmed by the extraordinary stability of this compound towards alkalis, its resistance to oxidation by aqueous potassium permanganate and the formation in almost quantitative yields of formaldehyde-phloroglucine complex by the action of a sulphuric acid solution of phloroglucine on the substance at 70° c (clowes. Tollens. Ber., 32, 2843 Ahm). Simple hydrolysis of the ether with 60 per cent sulphuric acid or decomposition with conc. hydriodic acid yielded only high melting resin-like solid products formed probably by a complex condensation between the liberated formaldehyde and the hydroxy benzyl-alcohol. Oxidation of this ether with chromic acid in acetic acid, however, yielded ultimately a nitro-salicylic acid,

m.p. 167° , different from all the three known (3-4-and 5-) nitro-salicylic acids. Hence the oxidation product was assumed to be 6-nitro-salicylic acid (IV) and consequently structure III was assigned to our reaction product.

6-nitro-salicylic acid has been incidentally found to be a sweet substance much sweeter than ortho-nitro-benzoic acid. The formation of the methylene ether (III) shows that the phenolic hydroxyl group has the predominating influence in directing the entrance of the oxymethyl group into the benzene nucleus; and that the steric effect of the nitro-group is more than counter-balanced by affinity and other factors.

THE REIMER-TIEMANN-REACTION.

Our experiments on this reaction with m-nitro-phenol and chloroform were conducted under a variety of conditions, but all gave us only very poor yields of aldehydic bodies (both steam-volatile and steam-nonvolatile). The volatile portion yielded an aldehyde V, m.p. $50-51^{\circ}$ identical with that reported by Robinson (J.C.S., 1930, 385).

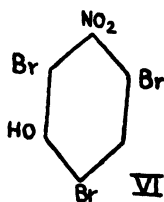


Its structure was guessed by Robinson from certain colour reactions to be 2-hydroxy, 6-nitro, benzaldehyde. We have got indications in confirmation of this by oxidising V to the sweet acid substance (IV), possibly identical with that obtained by the oxidation of the methylene ether (III). The same remarks, therefore, apply to this reaction with reference to the orienting influence of the nitro and phenolic groups.

THE MERCURIC ACETATE REACTION.

The mercuration of aromatic compounds has long been known to be as facile a reaction as nitration and halogenation (Whitmore, "Organic compounds of mercury", 1921). The mercuric acetate is usually dry heated with the aromatic compound at about 150° (Mameli, *Gazetta chim.*, 1922, 52, 1-27). We have found that the mercuration occurs with ease if an alcoholic solution of mercuric acetate is boiled for nearly an hour with meta-nitro-phenol on a boiling water-bath. The chief product of the reaction has been found to be a mono-acetoxy-mercuri-nitro-phenol melting at $207^{\circ}-208^{\circ}$. This yields on boiling with a solution of sodium chloride,

a chloro-mercuri-derivative (m.p. 179-181°). Determination of the position of the mercury-group by the usual method (Whitmore, J.A.C.S., 1926, 789) of displacing the mercury-group by bromine by reaction with conc. aqueous solution of potassium perbromide, resulted unexpectedly in the ready bromination of the mercurated nitro-phenol in two additional positions along with the replacement of the mercuri-group, yielding pure tribromo (2: 4: 6) 3-nitro-phenol (VI), a substance already known m. p. 87-88°.



It might be noted in this connection that meta-nitro-phenol itself does not yield the tribromo-derivative, except when heated in a sealed tube at 100°C. It therefore appears that the presence of the mercuri-group activates the other two positions in presence of bromine.

This result has enabled us only to state definitely that the acetoxy-mercuri-group should have occupied one of the three positions, 1, 4, or 6, proving again that it is the phenolic hydroxyl group that chiefly directs the orientation of the entering group in case of meta-nitro-phenol.

EXPERIMENTAL

Condensation of m-nitro-phenol with formaldehyde Formation of compound III

M-nitro-phenol (5g.) was taken in a round-bottom flask fitted with a reflux condenser, conc. hydrochloric acid (25 c.c.) and 40 per cent solution of formaldehyde (4g.) was added to it. The flask was heated in an oil-bath at 130°-40° for about 2 to 3 hours and was then allowed to cool. The supernatant clear liquid was poured off, and a sticky lump of a brown material which remained at the bottom was treated with 2N sodium hydroxide solution, till it was strongly alkaline. The liquid was filtered from the insoluble residue, the residue washed with a little water and crystallised from alcohol. It crystallised in colourless needles melting at 77° (yield: 0.85g) (Found: C, 53.3; 53.02; H, 4.2; 4.4; N, 7.15; 7.5 per cent. C₈ H₇ O₄ N requires C, 53.03; H, 3.8; N, 7.7 per cent). The molecular weight determination gave the mean value 176.2, 0.2203. in benzene solution giving a lowering of 0.73° in freezing point; the Molecular weight according to the formula C₈ H₇ O₄ N being 181. The compound is volatile with steam.

The sodium hydroxide filtrate, when acidified and extracted with ether gave a brown solid in aqueous suspension, and a thick brown liquid from the ether solution. These two products could not be easily purified and were not worked up.

ACETYLATION OF COMPOUND III

Acetic anhydride (excess) and sodium acetate were added to compound III (0.2g.) and the mixture heated under reflux in an oil-bath, for about two hours, poured into water, vigorously shaken, extracted with ether and ether distilled off. The unchanged substance was recovered. Attempts to acetylate the compound with acetic anhydride and pyridine, as well as with acetyl chloride were also fruitless, the substance being recovered unchanged in each case. The experiment proved the absence of any free hydroxyl group.

OXIDATION OF COMPOUND III : FORMATION OF ACID IV.

Chromic acid (1.5g.) was dissolved in hot glacial acetic acid (100 c.c.) and the solution added to the compound III in acetic acid solution in a round bottom flask and allowed to stand overnight. It was then heated under reflux on a boiling water bath (about 2 hours) till the mixture became green. It was then evaporated to dryness in an evaporating dish, made strongly alkaline with 2*N* sodium hydroxide solution, and extracted with ether to remove any unchanged material. The sodium hydroxide solution was filtered, acidified and extracted with ether, after saturating it with common salt. The ether extract on distillation left a black mass (0.2g.) which when dissolved in benzene, filtered and allowed to stand gave pure yellowish crystals m.p. 166°-7° C (0.15g.). The equivalent of the acid was found to be exactly the same as that of nitro-salicylic acid (183). Found : C, 46.1; H, 2.6; N, 7.62 per cent., C₇ H₅ O₅ N requires : C, 45.9 H, 2.7; N, 7.65 per cent. The acid was found to be extremely sweet.

CONDENSATION OF COMPOUND III WITH PHLOROGLUCIN.

0.231 gms. of the methylene-ether III was warmed in a water-bath at 80-90° C, for two hours with 30 c. c. of phloroglucinol-reagent (phloroglucinol, 3 gms; conc. sulphuric acid 60 c.c.; and water 200 c.c.). The red precipitate which was formed after allowing the mixture to stand overnight, was filtered

in a gooch crucible, washed with water and dried (yield 0.42g).

REIMER-TIEMANN REACTION APPLIED TO M-NITROPHENOL.

FORMATION OF ALDEHYDE V.

Chloroform (7 c.c.) was added to a solution of m-nitro-phenol (5g.) in water (35 c.c.) and sodium hydroxide (6.5g) and the mixture heated under reflux, on a water-bath for an hour. After the removal of excess of chloroform, the solution was acidified with dilute sulphuric acid and distilled in steam.

The distillate was saturated with common salt and extracted with ether. After the distillation of the ether, the crystalline residue was treated with a solution of sodium bisulphite, and ether extracted to remove non-aldehydic bodies. This ether extract gave unchanged m-nitro-phenol (1.1g.). The Sodium bisulphite solution on decomposition with conc. hydrochloric acid and extraction with ether, yielded a quantity of yellow crystals which on recrystallisation from petrol gave beautiful needles m.p. 50-51° c (0.05g).

The residue left in the flask after steam-distillation, was extracted with ether, the ether extract washed with a little water and then with sodium bisulphite solution. After washing it once more with a little water, ether was distilled off, which gave unchanged m-nitro-phenol (2.16g). The sodium bisulphite solution on being treated as before, gave a small quantity of an oil which became black on exposure and did not solidify completely. It was difficult to purify and was not further worked up.

OXIDATION OF THE ALDEHYDE V.

The aldehyde (0.05g) was taken in a conical flask and an aqueous solution of potassium permanganate (0.5g excess) added gradually. The flask was heated on a boiling water-bath, till no more of the permanganate was decolourised. The solution was made acidic, saturated with common salt and extracted with ether. The ether extract was washed with a dilute solution of sodium carbonate to remove acidic material. The sodium carbonate solution on being acidified and extracted with ether, gave after washing, drying, and distilling the ether from the extract, a very small quantity of a solid substance, which tasted very sweet.

CONDENSATION OF M-NITRO-PHENOL WITH MERCURIC ACETATE.

The products obtained by the mercuriation of m-nitro-phenol by dry-heating with mercuric acetate were rather cumbersome and the yields poor. It was therefore thought advisable to study the mercuriation in a solvent. Glacial acetic acid and alcohol were tried, the alcohol method proving very satisfactory.

A mixture of m-nitro-phenol (5g.), mercuric acetate (11.5g) and Parry's alcohol (100 c.c.) was boiled in a round bottom flask under reflux for half an hour, at the end of which the mixture was filtered hot from residue A (2.45g). The filtrate on cooling gave a quantity of yellow crystals (B) (m.p. $207^{\circ}-8^{\circ}$) which was filtered. The filtrate further gave a quantity of the same substance on concentration (Found : Hg, 50.1 ; C, H, O, N. Hg requires Hg, 50.39 per cent). The total yield of the substance (B) was about 7.0g.

The insoluble brownish red powder (A) turned black on treatment with 2N-alkali, and the filtered alkali solution gave no precipitate on acidification. This was rejected.

CONVERSION OF SUBSTANCE B (OBTAINED ABOVE) INTO
A CHLORO-MERCURI-DERIVATIVE AND SUBSEQUENT
BROMINATION

The substance B (5g.) was boiled gently with a 10 per cent solution of sodium chloride and filtered after cooling. The residue (4.2g) melted at $179-80^{\circ}\text{C}$.

The chloro-derivative (4.2g.) was placed in a round bottom flask and a 1.8N solution of bromine in potassium bromide solution was added to it gradually (40 c.c.), till no more bromine was absorbed. The operation was carried out entirely in the cold and in the first stages under ice-cooling. The mixture was left overnight, made alkaline the next day, and filtered. The filtrate was acidified, saturated with common salt and extracted with ether. On removing ether from the dried ether extract, a crystalline substance was obtained. This was dissolved in a minimum quantity of benzene and filtered. The benzene solution gave on standing beautiful yellowish needles m.p. $87^{\circ}-88^{\circ}$ (3.6g) which from its bromine percentage and m.p. was identified as 2 : 4 : 6-tri-bromo-3-nitro-phenol. (Found : Br, 63.3 : C, H, O, N, Br, requires Br, 63.8 per cent).

An attempt to prepare the mono-bromo-compound by using a restricted quantity of bromine resulted also in the formation of the tri-bromonitro-phenol in a smaller yield together with the unchanged material.

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TAUTOMERISM OF PHENYL-BUTENOIC ACIDS

By

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In the study of the influence of α -phenyl group in three carbon tautomerism (Phalnikar and Nargund, Jour. Ind. Chem. Soc. 1937, 736) it was shown that the phenyl group behaved like an alkyl group in depressing the mobility of the system and influenced the equilibrium by virtue of its conjugative effect. The present paper deals with the following systems:—

$\beta\gamma$ -diphenyl- Δ^a -butenoic acid $\rightleftharpoons$ $\beta\gamma$ -diphenyl- Δ^b -butenoic acid.
 $\alpha\beta$ -diphenyl- Δ^a -butenoic acid $\rightleftharpoons$ $\alpha\beta$ -diphenyl- Δ^b -butenoic acid.

Preparation of diphenyl-butenoic acids:— $\beta\gamma$ -diphenyl- β -hydroxy-butyric acid was obtained by the hydrolysis of ethyl- $\beta\gamma$ -diphenyl- β -hydroxy-butyrate obtained by the Reformatsky reaction of ethyl bromoacetate on desoxy benzoin. Heating $\beta\gamma$ -diphenyl- β -hydroxy-butyric acid with acetic anhydride (Wallach Ann., 1907, 353, 234.) gave $\beta\gamma$ -diphenyl- Δ^a -butenoic acid m.p. 126-127°. This was characterised by the preparation of an anilide m.p. 135° and p-toluidide m.p. 157°. Its constitution was proved by ozonisation when desoxy benzoin was the sole product obtained. The constitution is further confirmed by its low bromine value (*vide* expt.). Attempts to dehydrate ethyl- $\beta\gamma$ -diphenyl- β -hydroxy-butyrate, by potassium hydrogen sulphate, phosphorus oxychloride, and thionyl chloride and pyridine (compare Kon and Nargund J. C. S., 1932, 2461.) were unsuccessful. Phosphorus pentoxide, however readily dehydrated the hydroxy-ester and gave ethyl- $\beta\gamma$ -diphenyl- Δ^b -butenoate which on hydrolysis gave $\beta\gamma$ -diphenyl- Δ^b -butenoic acid, m.p. 173°. The high bromine value and the isolation of benzoic acid on oxidation confirms its structure. Its anilide had m.p. 172° and p-toluidide m.p. 160°. $\alpha\beta$ -diphenyl- β -hydroxy-butyric acid was obtained by the action of acetophenone on the grignard complex obtained from sodium phenyl acetate, Mg, and isopropyl bromide. (Ivanoff and Spasoff Bull. Soc. Chim 1931 (4), 49, 377-379). Dehydration of $\alpha\beta$ -diphenyl- β -hydroxy-butyric acid gave $\alpha\beta$ -diphenyl- Δ^a -butenoic acid m.p. 160°. Its constitution follows from the fact that on ozonisation it gave acetophenone and benzoic acid. All attempts to dehydrate ethyl- $\alpha\beta$ -diphenyl- β -hydroxy-butyrate were unsuccessful. Hence $\alpha\beta$ -diphenyl- Δ^b -butenoic acid could not be prepared. As the

equilibrium in this case is 100 per cent $\alpha\beta$, it is likely that $\alpha\beta$ -diphenyl- Δ^b -butenoic acid may not be capable of isolation.

Conditions of equilibration, and methods of calculations and estimations:—Standard conditions of Linstead (J. C. S., 1927, 2581.) were followed. The method of calculations has been given by Phalnikar and Nargund (loc. cit.). The iodometric method of Linstead and May (J. C. S., 1927, 2565) was inapplicable in the present case. Hence the bromometric method of Kon Linstead and Wright (J. C. S., 1934, 640) was followed. The results are given below:—

Acids	per cent of $\alpha\beta$ -isomeride at equilibrium	Mobility
$\beta\gamma$ -Diphenyl- Δ^a and- Δ^b . butenoic acids. ...	17	0.89
$\alpha\beta$ -Diphenyl- Δ^a -butenoic acid ...	100	...

Linstead and Williams (J. C. S., 1926, 2565) showed that a phenyl group stabilised exclusively the $\beta\gamma$ -isomeride. 17 per cent of $\alpha\beta$ -isomeride at equilibrium indicates the influence of a β -phenyl group. Existence of 100 per cent of $\alpha\beta$ -isomeride in $\alpha\beta$ -diphenyl butenoic acid confirms the conclusion of Goldberg and Linstead (J. C. S., 1928, 2343) that butenoic acids with no γ -substituents show no stability of $\beta\gamma$ -form even when substituted on β -carbon atom.

EXPERIMENTAL.

Desoxy-benzoin was prepared by the method given in "Organic Syntheses" (Vol. 12, page 16).

Ethyl- $\beta\gamma$ -diphenyl β -hydroxybutyrate:—Desoxy benzoin (75 gms.), Zn (27 gms.), ethyl bromoacetate (65 gms.) and benzene (300 c.c.) were allowed to react on steam bath. The mixture was then decomposed with ice and sulphuric acid, the benzene layer separated, washed, dried and benzene removed. Yield 90 gms. It was soluble in the usual solvents and crystallised best from a small quantity of petrol and had m.p. 60°. Mixed m.p. with desoxy benzoin was 48°. (Found: C, 75.9; H, 7.1 per cent. $C_{19}H_{20}O_2$, requires C, 76.1; H, 7.0 per cent).

$\beta\gamma$ -diphenyl- β -hydroxy-lutyric acid obtained by hydrolysis of the above ester by ten per cent solution of sodium hydroxide in cold was soluble in alcohol and chloroform and

sparingly in petrol and crystallised in needles from benzene, m.p. 126-127°. (Found: C, 74.8; H, 6.6 per cent. Eq. Wt., 255.7. $C_{16}H_{14}O_2$ requires C, 75.0; H, 6.3 per cent. Eq. Wt., 256).

$\beta\gamma$ -diphenyl- Δ^a -butenoic acid:— *$\beta\gamma$ -diphenyl- β -hydroxy-butyric-acid* (25 gms.) was refluxed with acetic anhydride (38 gms.) on a sand bath for three hours. Water was then added and acetic acid removed by steam distillation. The residue was treated with a solution of sodium bicarbonate, extracted with ether and acidified; yield 12 gms. It was soluble in all solvents and crystallised in needles from benzene or dilute alcohol and had m.p. 114°. (Found: C, 80.6; H, 6.0 per cent. Eq. Wt., 237.1; Ag. in the silver salt, 31.8 per cent. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9 per cent. Eq. Wt., 238. $C_{16}H_{13}O_2Ag$ requires Ag, 31.3 per cent).

Ozonisation of $\beta\gamma$ -diphenyl- Δ^a -butenoic acid:—The acid (2 gms.) was dissolved in chloroform (50 c.c.) and a current of ozonised oxygen passed for 24 hours. The solvent was removed and the ozonide decomposed by shaking with water and extracted with ether. The ether layer was washed with a dilute solution of sodium carbonate, dried and ether removed. The residue on purification had m.p. 60° and did not depress the m.p. of desoxybenzoin.

Anilide of $\beta\gamma$ -diphenyl- Δ^a -butenoic acid prepared by heating the acid with the requisite quantity of aniline at 180° for ten minutes crystallised from alcohol in needles m.p. 135°. (Found: N, 4.8 per cent. $C_{22}H_{19}ON$ requires N, 4.5 per cent). The *p-toulidide* prepared similarly crystallised in clusters of needles from dilute alcohol m.p. 156°. (Found N, 4.6 per cent. $C_{23}H_{21}ON$ requires N, 4.3 per cent). *Ethyl- $\beta\gamma$ -diphenyl- Δ^a -butenoate* prepared from the silver salt of the acid and ethyl iodide was a colourless liquid b.p. 210° at 10 mm. (Found: C, 81.1; H, 7.0 per cent. $C_{18}H_{15}O_2$ requires C, 81.2; H, 6.8 per cent).

$\beta\gamma$ -diphenyl- Δ^b -butenoic acid:—Ethyl- *$\beta\gamma$ -diphenyl- β -hydroxy-butyrate* (28 gms.), benzene (50 c.c.) and P_2O_5 (21 gms.) were refluxed on water bath for three hours. Ice was then added, benzene layer separated, washed and benzene removed. The residue on fractionation gave ethyl- *$\beta\gamma$ -diphenyl- Δ^b -butenoate* (12 gms.), b.p. 210-215° at 12 mm. It was hydrolysed in cold with ten per cent sodium hydroxide solution. *$\beta\gamma$ -diphenyl- Δ^b -butenoic acid* was soluble in benzene, ether, chloroform, and hot alcohol m.p. 173°. (Found: C, 80.7; H, 6.0 per cent. Eq. Wt., 236.7. Ag. in silver salt, 31.7 per cent. $C_{16}H_{14}O_2$ Ag. requires C, 80.7; H, 5.9 per cent. Eq. Wt. 238. $C_{16}H_{13}O_2Ag$ requires Ag, 31.3 per cent).

Oxidation of $\beta\gamma$ -diphenyl- Δ^b -butenoic acid:—The acid (2 gms.) was dissolved in a small quantity of sodium hydroxide and treated with a three per cent. solution of potassium permanganate (200 c.c.). MnO_2 was filtered off and the filtrate concentrated and acidified. The substance obtained was identified as benzoic acid by mixed m.p.

The anilide of $\beta\gamma$ -diphenyl- Δ^b -butenoic acid crystallised in plates from alcohol and had m.p. 172° (Found: N, 5.0 per cent. $\text{C}_{22}\text{H}_{19}\text{ON}$ requires N, 4.5 per cent.) *p-toulidide* crystallised in needles from alcohol and had m.p. 160 – 161° . (Found: N, 4.7 per cent. $\text{C}_{23}\text{H}_{21}\text{ON}$ requires N, 4.3 per cent.).

α - β -diphenyl β -hydroxy butyric acid:—It was prepared by the method of Ivanoff and Spasoff (loc. cit.) Ivanoff and Spasoff give the m.p. of $\alpha\beta$ -diphenyl- β -hydroxy butyric acid as 182° . It has been found that this acid melts at 192° (Found: C, 74.8; H, 6.5 per cent. Eq. Wt., 256.4. Ag in silver salt, 29.6 per cent. Calculated for $\text{C}_{16}\text{H}_{16}\text{O}_3$ C, 75.0; H, 6.3 per cent. Eq. Wt., 256.0. $\text{C}_{16}\text{H}_{16}\text{O}_3$ Ag requires Ag, 29.8 per cent).

α - β -diphenyl- Δ^a -butenoic acid:— $\alpha\beta$ -diphenyl- β -hydroxy butyric acid (10 gms.) was refluxed on sand bath with freshly distilled acetic anhydride (15 gms.) for three hours. Water was then added and acetic acid removed by steam distillation. $\alpha\beta$ -diphenyl- Δ^a -butenoic acid was soluble in alcohol, ether, benzene and chloroform. It crystallised in needles from a small volume of acetic acid and had m.p. 160° . (Found: C, 80.6; H, 6.1 per cent Eq. wt., 238.0. Ag in silver salt, 31.7 per cent. $\text{C}_{16}\text{H}_{14}\text{O}_2$ requires C, 80.7; H, 5.9 per cent. Eq. Wt., 238.0. $\text{C}_{16}\text{H}_{14}\text{O}_2$ Ag requires Ag, 31.3 per cent).

Ozonisation of $\alpha\beta$ -diphenyl- Δ^a -butenoic acid:—The acid (3 gms.) dissolved in chloroform (50 c. c.) and a current of ozonised oxygen passed through it for 24 hours. Chloroform was removed at ordinary temperature and the ozonide decomposed by water, extracted with ether, washed with sodium carbonate, dried and ether removed. The residue was converted into phenyl hydrazone by treatment with phenyl-hydrazine acetate. The phenyl hydrazone had m. p. 105° and was identified as acetphenone phenyl-hydrazone by mixed m.p. The sodium carbonate extract on acidifying gave a solid m.p. 121° which was identified as benzoic acid by mixed m.p.

Anilide of $\alpha\beta$ -diphenyl- Δ^a -butenoic acid prepared in the usual manner crystallised in needles from alcohol m.p. 148. (Found: N, 4.8 per cent. $\text{C}_{22}\text{H}_{19}\text{ON}$ requires N, 4.5 per cent).

Ethyl- $\alpha\beta$ -diphenyl- β -hydroxy butyrate.—It was prepared by esterification of $\alpha\beta$ -diphenyl- β -hydroxy-butyric acid with ethyl alcohol containing five per cent dry hydrogen chloride. It was a colourless liquid b.p. 130°C at 10 mm. (Found : C, 75.9 ; H, 7.3 per cent. $\text{C}_{18}\text{H}_{20}\text{O}_2$ requires C, 76.1 H, 7.0 per cent). All attempts to dehydrate this ester to get ethyl- $\alpha\beta$ -diphenyl- Δ^b -butenoate were unsuccessful.

The bromine addition method as described by Kon Linstead and Wright (local) was followed for the determination of mixture of unsaturated acids. The bromine value of pure acids as well as of mixtures of known composition were determined. The results are shown below. Data for the reference curve for the estimation of mixtures of $\beta\gamma$ -diphenyl- Δ^a -and- Δ^b -butenoic acids.

Tem. 30° Time 3 minutes

Per cent. of $\alpha\beta$ in the mixture	0	10	30	50	70	90	100
Per cent. of Br absorbed	46.7	44.9	43.0	35.5	22.7	13.0	8.0

Equilibrations of $\beta\gamma$ -diphenyl- Δ^a -and- Δ^b -butenoic acids.—The standard conditions of Linstead were followed. The equivalent weights of the recovered acids from the equilibration experiments were determined which showed that no addition of water to the double bond had taken place. The results are given in the following table :—

Acid	Time	Per cent of bromine addition of recovered acids	per cent of $\alpha\beta$	10 ($K_1 + K_2$)
$\alpha\beta$	5 hours	38.0	40	2.56
$\alpha\beta$	32 hours	40.1	35	0.447
$\beta\gamma$	5 hours	46.1	2	0.25
$\beta\gamma$	32 hours	45.1	10	0.28

The equilibrium was determined by boiling the acids with ten equivalents of 25 per cent potassium hydroxide solution in a

copper flask. The mean results of duplicate experiments are given in the following table:—

Acid	Time	Per cent of Br addition of recovered acid	Per cent $\alpha\beta$ at equilibrium
$\alpha\beta$	70 hours	44.3	16
$\beta\gamma$	70 hours	43.9	18

$\alpha\beta$ -diphenyl- Δ^a -butenoic acid:—To determine the equilibrium in this case it was boiled with ten equivalents of 25 per cent potassium hydroxide solution but the acid was recovered unchanged thus indicating that the equilibrium in this case is 100 per cent $\alpha\beta$.

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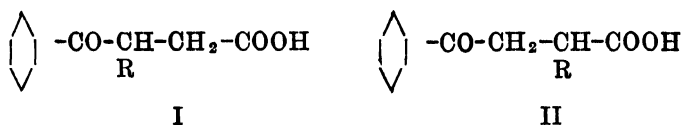
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CONDENSATION OF P-METHOXY-PHENYL-SUCCINIC-ANHYDRIDE WITH ANISOLE AND CRESOL METHYL ETHERS

By

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The anhydride of an unsymmetrically substituted succinic acid when condensed by Friedel and Crafts' reaction may be expected to yield two different γ -keto acids as shown below :—



Methyl-succinic-anhydride has been condensed with benzene by Meyer and Stann (B. 56, 1424). They isolated both the above types of keto acids. Mitter and De (Jour. Ind. Chem. Soc., 1939, 199) condensed methyl-succinic-anhydride with a number of phenol ethers and isolated only one type of keto acids *viz.* type II. Other substituted succinic-anhydrides have similarly yielded only products of the type II (Anschutz, Hahn and Walter. Ann. 1907, 354, 150. Desai and Wali. Proc. Ind. Acad. Sciences, 1937, 137. Robinson and Young, J. C. S., 1935, 1414). Wali, Desai, Muhammad and Hunter (J. C. S., 1937, 1013) isolated both the types of keto acids in the condensation of phenyl-succinic-anhydride with benzene. Desai & Wali (*loc. cit.*) again isolated both the keto acids in the condensation of phenyl-succinic-anhydride with toluene and further observed that in presence of nitro-benzene as solvent one product preponderated while in absence of nitrobenzene the other was the main substance. From the above it will be clear that though there are two possibilities yet both, of them may not be formed and the type of product may depend on the solvent used. In the present communication we have condensed p-methoxy-phenyl-succinic anhydride with anisole and cresol methyl ethers using different solvents.

Anisole and p-methoxy-phenyl-succinic-anhydride gave a keto acid m.p. 163° as the sole product of the reaction when either nitro-benzene or carbondisulphide was used as solvent. When acetylene tetrachloride was used as solvent the substance m.p. 163° was again the main product but was accompanied by another substance, m.p. 83° . The quantity of the latter being small it was not further investigated. The substance, m.p. 163° has been assigned the constitution α -p-methoxy-phenyl- β -p-methoxy benzoyl propionic acid on the following grounds: (1) It was synthesised by Hahn and Lapworth's method. (J. C. S., 1904, 1358). 4:4'-dimethoxy chalkone (Kuroda and Matsukama. Inst. Phys. Chem. Research. Tokyo, 1932, 18, 51) did not react with potassium cyanide under any conditions but the bromine addition product of the above chalkone *viz.* α -p-methoxy-phenyl- β -p-methoxy-benzoyl- α - β -dibromo ethane readily reacted with potassium cyanide and gave a cyano compound which on hydrolysis gave the keto acid, m.p. 163° . (Compare Dodwadmath and Wheeler Proc. Ind. Acad. Sciences, 1935, 438). (2) The keto acid m.p. 163° gave anisic acid as the sole product on oxidation. (3) It reacted with salicylic aldehyde in presence of hydrogen chloride to give a pyrylium derivative thus indicating the presence of $-\text{COCH}_3$ grouping. (Decker and Fallenberg. Ann., 1907, 356, 302, Perkin Robinson and Turner, J. C. S., 1908, 1085).

O-cresol-methyl-ether and p-methoxy-phenyl-succinic-anhydride gave the same keto acid m.p. 170° in different solvents. Its constitution *viz.* α -p-methoxy-phenyl- β -4-methoxy 3-methyl-benzoyl propionic acid follows from the following facts: (1) It could not be synthesised by Hahn and Lapworth's method as neither 4:4'-dimethoxy-3'-methyl chalkone nor α -p-methoxy-phenyl- β -4-methoxy-3-methyl benzoyl- α - β -dibromoethane reacted with potassium cyanide. A partial synthesis, however, by the action of p-methoxy phenyl succinic anhydride on the grignard reagent prepared from 2-methoxy-5-bromo toluene establishes the point of attachment. (2) The product reacted with salicylic aldehyde to give the pyrylium derivative.

M-cresol-methyl-ether and p-methoxy-phenyl-succinic anhydride gave a single product even in different solvents. Its constitution *viz.* α -p-methoxy-phenyl- β -4-methoxy-2-methyl-benzoyl propionic acid follows from the fact that it reacted with salicylic aldehyde to give a pyrylium derivative and it was synthesised by Hahn and Lapworth's method.

P-cresol-methyl-ether and p-methoxy-phenyl succinic-anhydride gave a keto acid, m.p. 168° when carbondisulphide or acetylene tetrachloride were used as solvents. In nitrobenzene as solvent the keto acid, m.p. 168° was accompanied by another isomeric acid, m.p. 198° . The constitution of the latter has not yet been established. The keto acid, m.p. 168° has been given the constitution α -p-methoxy-phenyl- β -2 methoxy-5-methyl benzoyl propionic acid as it reacted with salicylic aldehyde to give a pyrylium derivative and was identical with the product synthesised by the action of phenyl succinic anhydride on the grignard reagent prepared from 3-bromo-4-methoxy-toluene.

All the keto acids have been characterised by the preparation of derivatives such as methyl and ethyl esters.

EXPERIMENTAL

P-methoxy-phenyl-succinic acid was prepared by Baker and Lapworth's method (J.C.S., 1925, 565) with an important modification in the hydrolysis of the dicyano compound. Baker and Lapworth extracted the dicyano compound with ether and added to it a small amount of ethyl alcohol, saturated it with dry hydrogen chloride and then keeping it for some time continued the hydrolysis by boiling with concentrated hydrochloric acid. The product obtained was tarry and had to be purified by washing with ether. The modified process which consists in heating the dicyano compound with four parts of 25 per cent hydrochloric acid for eight hours on sand bath gives a cleaner product in quantitative yield. The anhydride was prepared by heating the acid with acetyl chloride on water bath and had m.p. 90.5° . General procedure for the condensation of p-methoxy-phenyl-succinic-anhydride with phenol ethers:—Anhydrous aluminum chloride (28 gms.) was added gradually to a mixture p-methoxy-phenyl-succinic-anhydride (0.1 mol.), the methyl ether (0.1 mol) and the solvent (100 cc.) kept in a round bottomed flask carrying a calcium chloride tube. The temperature was not allowed to go above 40° . It was kept at ordinary temperature for four hours, decomposed with ice and hydrochloric acid and the solvent removed by steam distillation. The solid obtained was purified by dissolving in a solution of sodium carbonate and reprecipitating by hydrochloric acid. The yields are given in the following table:—

Phenol ether used.	Product obtained	Per cent yield
Anisole ...	α -p-methoxy-phenyl- β -p-methoxy-benzoyl propionic acid.	95 per cent in acetylene tetrachloride. 35 per cent in CS_2 . 77 per cent in nitrobenzene.
o-cresol-methyl ether.	α -p-methoxy-phenyl- β -4-methoxy 3-methyl- benzoyl propionic acid.	95 per cent in acetylene te- trachloride. 65 per cent in CS_2 . 92 per cent in nitrobenzene.
m-cresol methyl ether.	α -p-methoxy phenyl- β -4-methoxy 2-methyl- benzoyl propionic acid.	90 per cent in acetylene tetrachloride. 15 per cent in CS_2 . 75 per cent in nitrobenzene.
p-cresol methyl ether.	α -p-methoxy phenyl- β -2-methoxy 5-methyl benzoyl propionic acid.	90 per cent in acetylene tetrachloride. 10 per cent in CS_2 . 45 per cent in nitrobenzene. There was another sub- stance obtained in 45 per cent yield in nitrobenzene.

α -p-methoxy-phenyl- β -p-methoxy benzoyl propionic acid:—It was soluble in chloroform and insoluble in petrol. It crystallised in small plates from alcohol m.p. 163° , (Found: C, 68.5; H, 5.9 per cent. Ag. in silver salt, 25.58 per cent. Eq. wt. 315.2. $\text{C}_{18}\text{H}_{18}\text{O}_5$ requires C, 68.8; H, 5.7 per cent. Eq. wt, 314. $\text{C}_{18}\text{H}_{17}\text{O}_5$ Ag. requires Ag, 25.65 per cent).

Oxidation of the above acid:—The acid (2 gms.) dissolved in a solution of sodium hydroxide was treated with KMnO_4 (3.1 gms.) dissolved in water (100 c.c.). It was warmed on water bath, filtered and the filtrate concentrated and acidified. The substance obtained had m.p. 180° and did not depress the m.p. of anisic acid.

Synthesis of the above acid:—preparation of 4-4'-dimethoxy chalkone: p methoxy acetophenone (2 gms.) and anisaldehyde (2 gms.) were dissolved in alcohol (20 c.c.) and warmed. 50 per cent sodium hydroxide solution (4 gms.) was gradually added and the whole heated on water bath for ten minutes; yield 3 gms.; it crystallised in plates from alcohol and had m.p. 105° . It did not react with potassium cyanide. Kuroda and Matsukama Inst. Phys. Chem. Research. Tokio, 1932, 18, 51 give the m.p. of 4-4'-dimethoxy chalkone as 100° .

α -p-methoxy-phenyl- β -p-methoxy benzoyl- α - β -dibromo ethane:—It was prepared by adding bromine (3 gms.) dissolved in CS_2 (15 c.c.)

to a solution of 4-4'-dimethoxy chalcone (5 gms.) in CS_2 (15 c.c.) The substance obtained on removing CS_2 was crystallised from benzene and petrol m.p. 150° with slight decomposition. (Found: Br, 37.8 per cent. $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Br}_2$ requires Br, 37.4 per cent). The bromo compound (7 gms.) potassium cyanide (3.5 gms.) and alcohol (35 c.c.) were refluxed together on steam bath for three hours. Alcohol was removed, diluted with water acidified and extracted with ether dried and ether removed. The residue which was a thick liquid was dissolved in Con. H_2SO_4 (15 c.c.) diluted with water till a slight turbidity appeared and then boiled on sand bath for four hours. The product thus obtained on purification had m.p. 160° and did not depress the m.p. of α -p-methoxy-phenyl- β -p-methoxy-benzoyl propionic acid.

Pyrylium derivative of α -p-methoxy-phenyl- β -p-methoxy-benzoyl propionic acid:—A solution of the acid (1 gm.) salicylic aldehyde (1 gm.) in methyl alcohol (50 c.c.) was cooled in ice and saturated with dry hydrogen chloride. It was then left overnight and then poured in alcohol containing HCl. The crimson red ppt thus obtained was filtered and washed with alcohol. It did not melt up to 290° and was insoluble in dilute sodium hydroxide solution.

Methyl- α -p-methoxy-phenyl- β -p-methoxy-benzoyl propionate obtained by esterifying the acid with methyl alcohol was soluble in benzene, chloroform and ethyl acetate and hot ethyl alcohol and insoluble in petrol. It crystallised in small plates from alcohol and had m.p. 98° . (Found: C, 69.2; H, 6.2 per cent. $\text{C}_{19}\text{H}_{20}\text{O}_5$ requires C, 69.5; H, 6.1 per cent).

Ethyl- α -p-methoxy-phenyl- β -p-methoxy-benzoyl propionate prepared similarly crystallised in thin long plates from alcohol and had m.p. 85° . (Found: C, 70.0; H, 6.5 per cent. $\text{C}_{21}\text{H}_{22}\text{O}_5$ requires C, 70.2; H, 6.4 per cent).

α -p-methoxy-phenyl- β -4-methoxy-3-toluoyl propionic acid:—It was soluble in hot alcohol, ethyl acetate, hot benzene and insoluble in petrol. It crystallised in thin rectangular plates from alcohol and had m.p. 170° . (Found: C, 69.3; H, 6.2 per cent. Eq. wt, 330.0. Ag in silver salt, 24.7 per cent. $\text{C}_{19}\text{H}_{20}\text{O}_5$ requires C, 69.5; H, 6.1 per cent. Eq. wt., 328.0. $\text{C}_{19}\text{H}_{19}\text{O}_5\text{Ag}$ requires Ag, 24.8 per cent). 3-methyl-4-methoxy acetophenone was prepared by methylating 3-methyl-4-hydroxy acetophenone (Nencki and Stober B, 30, 1770) with dimethyl sulphate and ten per cent sodium hydroxide solution. It was a colourless liquid b.p. 260 – 265 at ordinary pressure. (Found: C, 73.7; H, 7.5 per cent. $\text{C}_{10}\text{H}_{12}\text{O}_2$

requires C, 73.9; H, 7.4 per cent). 4-4'-dimethoxy-3'-methyl chalkone prepared from the above ketone and anisaldehyde was oily and could not be obtained in crystalline condition. It, however, gave crystalline α -p-methoxy-phenyl- β -3-methyl-4-methoxy-benzoyl- α - β -dibromo ethane on treating with the requisite quantity of bromine. The dibromo compound had m.p. 121°. (Found : Br, 36.6 per cent. $C_{18}H_{18}O_3Br_2$ requires Br, 36.2 per cent). Neither the chalkone nor the dibromo compound reacted with potassium cyanide.

Partial synthesis of α -p-methoxy phenyl- β -4-methoxy-3-toluoyl propionic acid:—2-methoxy-5-bromo toluene was prepared by methylating 2-hydroxy-5-bromo toluene of Claus and Jackson (J. Pr. Chem. 238, 324). It had b.p. 110°-115° at 10 mm. (Found: Br, 40.1 per cent. C_8H_9OBr requires Br, 39.8 per cent). To a hot solution of p-methoxy-phenyl-succinic anhydride (4 gms.) in benzene (20 c.c.) was added the grignard reagent prepared from 2-methoxy-5-bromo toluene (4 gms.), Mg, (0.4 gms.) and dry ether (20 c.c.). On working in the usual way the substance had m.p. 170° and did not depress the m.p. of α -p-methoxy phenyl- β -4-methoxy-3-toluoyl propionic acid. Methyl- α -p-methoxy-phenyl- β -4-methoxy 3-toluoyl propionate was soluble in benzene, chloroform, ethyl acetate and hot ethyl alcohol from which it crystallised in plates m.p. 98°. (Found: C, 70.0; H, 6.6 per cent. $C_{20}H_{22}O_5$ requires C, 70.2; H, 6.4 per cent). Ethyl- α -p-methoxy phenyl- β -4-methoxy-3-toluoyl propionate had similar solubilities and crystallised from alcohol in plates m.p. 82°. Found: C, 70.6; H, 6.9 per cent. $C_{22}H_{24}O_5$ requires C, 70.8; H, 6.7 per cent).

α -p-methoxy-phenyl- β -4-methoxy-2-toluoyl propionic acid. It was soluble in hot alcohol, benzene, ethyl acetate, acetic acid and insoluble in petrol. It crystallised in needles from alcohol, m.p. 148°. (Found: C, 69.2; H, 6.3 per cent. Ag, in silver salt, 24.7 per cent. $C_{19}H_{20}O_5$ requires C, 69.5; H, 6.1 per cent. $C_{19}H_{19}O_5$ Ag requires Ag, 24.8 per cent).

Synthesis of the above acid:—Preparation of 4-4'-dimethyl-2'-methyl chalkone. 4-methoxy-2-methyl acetophenone (2 gms.), anisaldehyde (2 gms.) were dissolved in alcohol (20 c.c.) and a few drops of ten per cent sodium hydroxide solution were added and warmed on a water bath for half an hour. The chalkone obtained on pouring it in water crystallised in small plates from chloroform and petrol m.p. 147°. (Found: C, 76.5; H, 6.5 per cent. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4 per cent). α -p-methoxy phenyl- β -4-methoxy-2-toluoyl- α - β -dibromo ethane prepared by

adding the requisite quantity of bromine to the above chalkone was insoluble in alcohol, petrol and soluble in hot ethyl acetate from which it crystallised in dirty white needles m.p. 160° . (Found: Br, 36.5 per cent; $C_{18}H_{18}O_2Br_2$ requires Br, 36.2 per cent). The above bromo compound (16 gms.) potassium cyanide (6 gms.) absolute alcohol (80 c.c.) and water (4 c.c.) were refluxed on a steam bath for three hours and then worked as described under the synthesis of the keto acid from anisole. The substance obtained had m.p. 145° and did not depress the m.p. of the product obtained from m-cresol-methyl ether.

Methyl- α -p-methoxy-phenyl- β -4-methoxy-2-toluoyl propionate was a colourless liquid b.p. $210-215$ at 8 m.m. (Found: C, 69.9; H, 6.5 per cent. $C_{20}H_{22}O_6$ requires C, 70.2; H, 6.4 per cent). Pyrylium derivative of α -p-methoxy-phenyl- β -4-methoxy-2-toluoyl propionic acid prepared as usual was deep red in colour, insoluble in dilute sodium hydroxide solution and did not melt up to 300° .

α -p-methoxy-phenyl- β -2-methoxy-5-toluoyl propionic acid:—This was soluble in ethyl acetate hot alcohol chloroform, slightly soluble in hot benzene and insoluble in petrol. It crystallised from alcohol in tiny plates m.p. 168° . (Found: C, 69.3; H, 6.1 per cent. Eq. wt. 326.3. $C_{19}H_{20}O_6$ requires C, 69.5; H, 6.1 per cent, Eq. wt. 328).

2-methoxy-5-methyl acetophenone prepared by methylating 2-hydroxy-5-methyl acetophenone (Auwers. Ann, 364, 166) by dimethyl sulphate and ten per cent sodium hydroxide solution was a colourless liquid b.p. 120° at 8 m.m. and 254° at ordinary pressure. (Found: C, 74.0; H, 7.5 per cent. $C_{10}H_{12}O_2$ requires C, 73.9; H, 7.4 per cent). All attempts to prepare a chalkone from the condensation of the above ketone with anisaldehyde were fruitless.

Partial synthesis of α -p-methoxy-phenyl- β -2-methoxy-5-toluoyl propionic acid:—To a hot solution of p-methoxy-phenyl-succinic anhydride (4 gms.) in benzene (40 c.c.) was added the grignard reagent prepared from 3-bromo-4-methoxy-toluene (Schall and Dralle. B. 17, 2531). (4 gms.) Mg, (0.5 gms.) and dry ether (25 c.c.). Ice was then added and the acid isolated in the usual manner was washed with hot water to remove p-methoxy-phenyl-succinic acid. The residue on crystallisation had m.p. 168° and did not depress the m.p. of the product from p-cresol-methyl ether.

Methyl- α -p-methoxy-phenyl- β -2-methoxy-5-toluoyl propionate prepared in the usual manner was a colourless liquid b.p. 250 at 18 mm. (Found: C, 70.0; H, 6.6 per cent. $C_{20}H_{22}O_5$ requires C, 70.2; H, 6.4 per cent).

Ethyl- α -p-methoxy-phenyl- β -2-methoxy-5-toluoyl propionate was soluble in benzene, chloroform, ethyl acetate and hot alcohol. It had m.p. 95°. (Found: C, 70.6; H, 6.9 per cent. $C_{22}H_{24}O_5$ requires C, 70.8; H, 6.7 per cent).

The pyrylium derivative of α -p-methoxy-phenyl- β -2-methoxy-5-toluoyl propionic acid was deep red in colour and did not melt up to 300°.

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CONDENSATION OF P-METHOXY-PHENYL-SUCCINIC-ANHYDRIDE WITH THE METHYL ETHERS OF CATECHOL, RESORCINOL AND HYDROQUINONE.

By

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The present work is a continuation of the preceding paper. Veratrole when condensed with p-methoxy-phenyl-succinic anhydride gave α -p-methoxy-phenyl- β -3 : 4-dimethoxy-benzoyl-propionic acid the constitution of which follows from the fact that it gave a pyrylium derivative and was identical with the substance obtained by the action of potassium cyanide on α -p-methoxy-phenyl- β -3 : 4-dimethoxy-benzoyl- α - β -dibromo ethane and subsequent hydrolysis. Guaiacol did not condense. Resorcinol dimethyl ether gave α -p-methoxy-phenyl- β -2 : 4-dimethoxy benzoyl propionic acid. This keto acid could not be synthesised from 4 : 2' : 4'-trimethoxy chalcone or its bromine addition product. The same acid could, however, be prepared by the action of p-methoxy-phenyl-succinic anhydride on the grignard reagent prepared from 4-iodo resorcinol dimethyl ether. It gave deep red pyrylium derivative when treated with salicylic aldehyde. Resorcinol monomethyl ether gave α -p-methoxy-phenyl- β -2-hydroxy-4-methoxy-benzoyl-propionic acid the constitution of which follows from the fact that on methylation it gave a trimethoxy keto acid identical with the acid obtained from resorcinol dimethyl ether and p-methoxy-phenyl-succinic anhydride. That the side chain— $\text{COCH}_2\text{CH}_2\text{COOH}$ —is in ortho position to hydroxyl group is inferred from the fact that it gave bluish colouration with a solution of ferric chloride. In common with other acids it also gave deep red pyrylium derivative.

Hydroquinone-dimethyl ether gave α -p-methoxy-phenyl- β -2 : 5-dimethoxy-benzoyl propionic acid also synthesised from α -p-methoxy-phenyl- β -2 : 5-dimethoxy-benzoyl- α - β -dibromo ethane. Hydroquinone did not condense with p-methoxy-phenyl-succinic anhydride under any conditions.

EXPERIMENTAL.

The yields of keto acids obtained by following the procedure described in the preceding paper are given in the following table:—

Phenol ether used	Product obtained	Yield in different solvents
Veratrole.	α -p-methoxy-phenyl β -3: 4-dimethoxy-benzoyl propionic acid.	64 per cent in nitrobenzene. 85 per cent in acetylene tetrachloride. No reaction in CS_2 .
Guaicol.	No reaction in any solvent.	
Resorcinol dimethyl ether.	α -p-methoxy-phenyl β -2: 4-dimethoxy benzoyl propionic acid.	64 per cent in nitrobenzene. 43 per cent in acetylene tetrachloride. 95 per cent in CS_2 .
Resorcinol monomethyl ether.	α -p-methoxy-phenyl β -2: hydroxy-4-methoxy-benzoyl propionic acid.	69 per cent in nitrobenzene. 78 per cent in acetylene tetrachloride. 21 per cent in CS_2 .
Hydroquinone dimethyl ether.	α -p-methoxy-phenyl β -2: hydroxy-4-methoxy-benzoyl propionic acid.	29 per cent in nitrobenzene. 14 per cent in acetylene tetrachloride. No reaction in CS_2 .
Hydroquinone monomethyl ether.	No reaction in any solvent.	

α -p-methoxy-phenyl- β -3 : 4-dimethoxy-benzoyl-propionic acid was soluble in hot alcohol, hot acetic acid, but insoluble in benzene, ethyl acetate, petrol and carbondisulphide. It crystallised in granules from alcohol and had m.p. 188° . Ba and Ca salts were insoluble while Ag salt was insoluble in cold but soluble in hot water. (Found : C, 66.7 ; H, 5.8 per cent. Eq. Wt., 341. Ag. in silver salt, 24.2 per cent. $\text{C}_{19}\text{H}_{20}\text{O}_6$ requires C, 66.3 ; H, 5.8 per cent. Eq. Wt., 344. $\text{C}_{19}\text{H}_{19}\text{O}_6\text{Ag}$. requires Ag. 23.9 per cent).

Synthesis of the above acid:—4 : 3' : 4'-trimethoxy chalkone prepared by the method of Kauffmann and Kieser (B, 46, 3798). did not react with potassium cyanide. α -p-methoxy-phenyl- β -3 : 4-dimethoxy-benzoyl- α - β -dibromo ethane prepared by adding the requisite quantity of bromine to the above chalkone crystallised in rosettes of needles from acetic acid, m.p. 138° . The bromo-compound (3 gms.), potassium cyanide (1.5 gms.) and alcohol (18 c.c.) were refluxed together on water bath for three hours. Alcohol was removed and the cyano compound isolated and

mixture was heated on water bath for ten minutes. The yellow solid obtained was soluble in chloroform, hot alcohol and hot acetic acid. It crystallised in prisms from acetic acid m.p. 99°. (Found: C, 72.4; H, 6.2 per cent. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.0 per cent.). This chalcone did not react with potassium cyanide.

α-p-methoxy-phenyl-β-2:5-dimethoxy benzoyl-α-β-dibromothane prepared by the addition of the theoretical quantity of bromine to the above chalcone crystallised from acetic acid in plates m.p. 112°. (Found: Br, 35.2 per cent. $C_{18}H_{18}O_4Br_2$ requires Br, 34.9 per cent.). The bromo compound (5 gms.) potassium cyanide (3 gms.) and alcohol (20 c.c) were refluxed together and worked up as usual. The keto acid isolated had m.p. 168° and did not depress the m.p. of the condensation product.

Methyl-α-p-methoxy-phenyl-β-2:5-dimethoxy-benzoyl propionate was prepared by the interaction of the silver salt of the acid and methyl iodide. It crystallised in long needles from alcohol m.p. 102°. (Found: C, 66.9; H, 6.2 per cent. $C_{20}H_{22}O_6$ requires C, 67.0; H, 6.1 per cent.). *Ethyl-α-p-methoxy-phenyl-β-2:5-dimethoxy-benzoyl propionate* similarly prepared crystallised in needles from alcohol m.p. 75°. (Found: C, 67.7; H, 6.8 per cent. $C_{22}H_{24}O_6$ requires C, 67.7; H, 6.5 per cent.). *Semicarbazone of α-p-methoxy-phenyl-β-2:5-dimethoxy-benzoyl propionic acid* crystallised in needles from alcohol m.p. 126°. (Found: N, 10.8 per cent. $C_{20}H_{22}O_6N_2$ requires N, 10.5 per cent.).

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CONDENSATION OF SUCCINIC ANHYDRIDE WITH THE METHYL ETHERS OF ORCINOL AND PYROGALLOL

By

G. A. DALAL, K. V. BOKIL AND K. S. NARGUND.

The present work is a continuation of previous work (Dalal and Nargund, Jour. Ind. Chem. Soc., 1937, 408). Orcinol dimethyl ether and succinic anhydride in nitrobenzene, or carbondisulphide or acetylene tetrachloride gave β -2 : 4 : dimethoxy-6-methyl-benzoyl-propionic acid the constitution of which could not be confirmed either by oxidation or by its attempted synthesis from bromo-orcinol-dimethyl ether. Orcinol monomethyl ether and succinic anhydride gave β -2-methoxy-4-hydroxy-6-methyl-benzoyl propionic acid. Its constitution rests on the facts that on methylation it gave a product identical with the product obtained from orcinol dimethyl ether and that it did not give any colour reaction with aqueous or alcoholic ferric chloride thus indicating that in all probability the side chain— $\text{COCH}_2\text{CH}_2\text{COOH}$ —is not in ortho position to the hydroxyl group. Pyrogallol trimethyl ether and succinic anhydride gave β -2-hydroxy-3:4 : dimethoxy-benzoyl propionic acid in agreement with the work of Mitter and De (Jour. Ind. Chem. Soc., 1939, 35). That the free hydroxyl group in this acid could not be methylated by dimethyl sulphate and sodium hydroxide solution under any conditions is an argument in favour of the structure assigned to it.

EXPERIMENTAL

The yields of the keto-acids from the condensations as described by Dalal and Nargund (loc. cit.) are given below :—

Phenol ether used	Product obtained	Yield in different solvents
Orcinol dimethyl ether.	β -2 : 4 : dimethoxy-6-methyl-benzoyl-propionic acid.	40 per cent in CS_2 . 60 per cent in nitrobenzene. 45 per cent in acetylene tetrachloride.
Orcinol mono methyl ether.	β -2-methoxy-4-hydroxy-6-methyl-benzoyl-propionic acid.	25 per cent in nitrobenzene.
Pyrogallol trimethyl ether.	β -2-hydroxy-3 ; 4-dimethoxy-benzoyl propionic acid.	20 per cent in CS_2 . 45 per cent in nitrobenzene. 60 per cent in acetylene tetrachloride.

β -2-4-dimethoxy-6-methyl-benzoyl propionic acid. It was soluble in chloroform, alcohol, ethyl acetate and acetic acid. It melted under hot water in which it is slightly soluble. It crystallised from benzene in needles m.p. 120° . (Found: C, 61.9; H, 6.4 per cent. Eq. wt. 251.7. $C_{15}H_{16}O_5$ requires C, 61.7; H, 6.5 per cent. Eq. wt. 252). Ag, Pb and Ca salts were insoluble while Ba salt was soluble in hot water. *Methyl β -2-4-dimethoxy-6-methyl-benzoyl propionate* was a colourless liquid b.p. 160° at 16 mm. (Found: C, 63.1; H, 6.9 per cent. $C_{14}H_{18}O_5$ requires C, 63.2; H, 6.8 per cent). *Ethyl β -2-4-dimethoxy-6-methyl-benzoyl propionate* was also a liquid b.p. 170° at 20 m.m. (Found: C, 64.1; H, 7.4 per cent. $C_{15}H_{20}O_5$ requires C, 64.3; H, 7.1 per cent).

β -2-methoxy-4-hydroxy-6-methyl-benzoyl-propionic acid:—It was soluble in chloroform, alcohol, ethyl acetate, acetic acid and hot water, but insoluble in petrol. It crystallised in needles from ethyl acetate and petrol and had m.p. 145° . When it was crystallised from hot water the m.p. was rather low *viz.* 125° . Ca, Ag and Pb salts were insoluble while Ba salt was soluble in water. It gave no colour with ferric chloride. (Found: C, 60.3; H, 6.1 per cent. Ag in silver salt, 32.1 per cent. $C_{12}H_{14}O_5$ requires C, 60.5; H, 5.9 per cent. $C_{12}H_{13}O_5Ag$ requires Ag, 31.3 per cent). On methylation it gave *β -2:4-dimethoxy-6-methyl-benzoyl-propionic acid.*

β -2-hydroxy-3:4-dimethoxy-benzoyl-propionic acid:—It had m.p. 153° . Mitter and De (loc cit.) give m.p. 152° . Semicarbazone of the above acid prepared in the usual manner crystallised in fine needles from hot water and had m.p. 185° . (Found: N, 13.8 per cent. $C_{13}H_{17}O_5N_2$ requires N, 13.5 per cent).

Methyl- β -2-hydroxy-3:4-dimethoxy-benzoyl-propionate was soluble in chloroform, alcohol and ethyl acetate. It crystallised in needles from dilute alcohol m.p. 110° . (Found: C, 58.1; H, 6.1 per cent. $C_{13}H_{16}O_6$ requires C, 58.2; H, 5.9 per cent).

Ethyl- β -2-hydroxy-3:4-dimethoxy-benzoyl-propionate had similar solubility and crystallised from dilute alcohol in tiny needles m.p. 58. (Found: C, 59.5; H, 6.5 per cent. $C_{14}H_{18}O_6$ requires C, 59.6; H, 6.3 per cent).

We thank the University of Bombay for research grant to one of us (K. S. N.) and the Charak Trust for a gift of chemicals.

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THE CONDENSATION OF α -SUBSTITUTED ACETOACETATES WITH PHENOLS. PART II. USE OF VARIOUS CONDENSING AGENTS WITH ETHYL α -ACETOGLUTARATE.

By

N. M. SHAH

In Part I of this series (N. M. Shah and R. C. Shah, Ber, 1938, 71, 2075) it has been shown that ethyl α -acetoglutarate reacts with phenols in presence of sulphuric acid (Pechmann reaction) to form coumarin-3-propionic acid derivatives.

Chakravarti (J. Indian C. S., 1931, 8, 129, 407, 619 ; 1932, 9, 25, 31, 389 *et seq*) and Robertson and co-workers (J. C. S., 1931, 1256, 1877, 2426 ; 1932, 1180, 1681) have shown that coumarins are produced using sulphuric acid as a condensing agent if the reaction takes place but phosphoric anhydride (Simonis reaction) may produce either coumarins or chromones, depending upon the nature of the phenol used. Reactive phenols like resorcinol, pyrogallol, α -naphthol, orcinol invariably give coumarins irrespective of the condensing agent. Less reactive phenols like phenol, cresols, β -naphthol etc. give coumarins in poor yield with sulphuric acid ; with phosphoric anhydride produce chromones with α -alkyl acetoacetates.

The work described in this part was, therefore, undertaken with a view to study the effect of the change of the condensing agent on the course of the reaction with ethyl α -acetoglutarate already mentioned above. Phosphoric anhydride (Simonis reaction), phosphoric acid, anhydrous aluminium chloride and hydrochloric acid gas have been tried as condensing agents.

Resorcinol on condensation with ethyl α -acetoglutarate in presence of either phosphorus pentoxide, phosphoric acid or aluminium chloride produced 7-hydroxy-4-methylcoumarin-3-propionic acid in all cases. It is noteworthy that aluminium chloride as a condensing agent affords a high yield (*cf.* Sethna, Shah and Shah, Curr. Sc. 1937, 6, 93). Pyrogallol was condensed using phosphorus pentoxide as condensing agent but no definite product could be isolated from the reaction mixture. This is in conformity with the observations of Chakravarti (*loc. cit.*) and Robertson (*loc. cit.*) that the reaction of pyrogallol in presence of phosphorus pentoxide does not take place as the alkyl substituent increases in weight. α -naphthol and *m*-cresol could not be condensed in presence of phosphoric acid and hydrochloric acid gas

respectively. Orcinol gave 5-hydroxy-4:7-dimethylcoumarin-3-propionic acid with hydrochloric acid gas or phosphorus pentoxide as condensing agent. β -naphthol and p-cresol did not condense either in presence of phosphorus pentoxide or aluminium chloride.

From the above results, it can be safely concluded that the effect of change of condensing agent in the condensation of α -acetoglutaric ester with phenols has revealed no marked influence on the course of the reaction. The conclusions arrived at by previous investigators are applicable in this case too. The effect of the α -substituent, $-\text{CH}_2\text{CH}_2\text{COOEt}$ in α -acetoglutaric ester is comparable to that of $-\text{C}_6\text{H}_7$ in ethyl α -propyl acetoacetate with regard to phosphorus pentoxide.

A systematic study of ethyl acetosuccinate as well as of other acetoacetates with heavy α -substituents with a view to observe the effect of the substituent on the course of reaction is in progress.

EXPERIMENTAL

Condensation of resorcinol with ethyl α -acetoglutarate in presence of different condensing agents.

1. *In presence of phosphorus pentoxide*—To the mixture of resorcinol (3 g. : 1 mol.) and ethyl α -acetoglutarate (6 g. : 1 mol.), phosphorus pentoxide (10 g.) was added and the mixture heated on water-bath for about 2 hours. A pasty mass was obtained, which was repeatedly washed with water, basified with cold dil. NaOH, washed with acidulated water and finally with water, when it began to solidify. The solid was collected, treated with 2N NaOH and filtered. The filtrate on acidification gave a substance which after crystallisation from dil. alcohol melted at 224° not depressed by mixture with 7-hydroxy-4-methylcoumarin-3-propionic acid (Shah and Shah, Ber. 1938, 71, 2075).

2. *In presence of phosphoric acid*—To the above mixture of resorcinol and the ester, glacial phosphoric acid (25 c.c.) was added and kept for 2 days at room temperature. On pouring the reaction mixture into ice-cold water, a pasty mass was obtained, which was repeatedly washed with water. It was washed with dil. NaOH and filtered; a small quantity of a white substance was got, which on crystallisation from alcohol proved to be ethyl 7-hydroxy-4-methylcoumarin-3-propionate, m.p. and mixed m.p. 124° . (Shah and Shah, loc. cit.). The filtrate on acidification gave 7-hydroxy-4-methylcoumarin-3-propionic acid identical with the product mentioned above.

3. *In presence of anhydrous aluminium chloride*—To the solution of AlCl_3 (7 g. : 2 mols.) in dry nitrobenzene (40 c.c.), the

mixture of resorcinol and α -acetoglutarate was added and the mixture protected from moisture (CaCl_2 guard-tube) heated at $120-125^\circ$ till HCl gas evolution had subsided ($1-1\frac{1}{2}$ hours). It was cooled, ice and conc. HCl (15 c.c.) added and nitro-benzene steam-distilled off. The remaining liquid was freed from some tarry matter and the filtrate on cooling began to deposit crystals, m.p. and mixed m.p. 224° , identical with 7-hydroxy-4-methyl-coumarin-3-propionic acid. Yield, 5g.

Condensation of Orcinol with ethyl α -acetoglutarate in presence of different condensing agents.

1. *In presence of hydrochloric acid gas*—Orcinol (2g.) and the ester (3g.) were dissolved in alcohol (25 c.c.): the solution being cooled by ice, dry HCl gas was passed till it was saturated. The reaction mixture was then left at room temperature for 3 days. It was then poured into cold water; the separated solid was crystallised from alcohol; the melting point indicated that the product was not pure. On repeated crystallisations, the substance was obtained, m.p. $162-163^\circ$, the mixed m.p. with ethyl 5-hydroxy-4 : 7-dimethyl-coumarin-3-propionate (Shah and Shah, loc. cit.) not being depressed.

The acid mother-liquor on keeping gave a small quantity of the acid identical with 5-hydroxy-4 : 7-dimethylcoumarin-3-propionic acid (loc. cit.). Both the ester and the acid dissolve in alkali with yellow colour without fluorescence, characteristic of a 5-hydroxy-coumarin derivative.

2. *In presence of phosphorus pentoxide*—To the above mixture of orcinol and the ester, phosphorus pentoxide (10 g.) was added and the reaction mixture treated as in case of the resorcinol already described. The solid on crystallisation gave 5-hydroxy-4 : 7-dimethyl-coumarin-3-propionic acid (loc. cit.).

Other phenols did not condense or no definite product could be isolated with the condensing agent or agents given in parenthesis: Pyrogallol (phosphorus pentoxide), α -Naphthol (P_2O_5 , Phosphoric acid), β -Naphthol (P_2O_5 , AlCl_3), m- and p-cresols (any condensing agents):.

I am thankful to Dr. R. C. Shah for his kind interest and ungrudging help and to the University of Bombay for a research grant.

CHEMISTRY OF β -ARYL-GLUTACONIC ACIDS

PART V : $\alpha\gamma$ -C-diacetylation of β -aryl-glutaconic anhydrides : *A new method of synthesis of diphenyl derivatives*

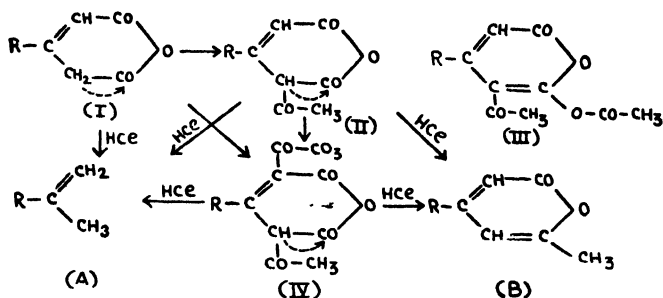
By

G. R. GOGTE

In part IV of this series¹, (Gogte, Proc. Ind. Acad. Sci. (A), 1938, 7, (214), β -aryl-glutaconic anhydrides (I) had been shown to get acetylated by acetic anhydride and fused sodium acetate or by acetyl chloride and pyridine, the products being α -C-acetyl- β -aryl-glutaconic anhydrides (II) with the acetyl group attached to the methylene carbon atom of the glutaconic anhydride. The titratability and ferric chloride colouration of these α -C-acetyl- β -aryl-glutaconic anhydrides also were attributed to the hydroxy group arising out of the wandering of the mobile hydrogen atom to the neighbouring carbonyl group. This naturally led to the expectation that these α -C-acetyl- β -aryl-glutaconic anhydrides (II) could further be acetylated to give neutral O-acetyl derivatives (III). Actually, further acetylation of these α -C-acetyl- β -aryl-glutaconic anhydrides (II), or acetylating the original β -aryl-glutaconic anhydrides (I) under energetic conditions using excess of the acetylating agents, has been observed to lead to compounds indicating no doubt the entry of one more acetyl group in the α -C-acetyl- β -aryl-glutaconic anhydride, but even these titrated as strong monobasic acids and gave pronounced colourations with ferric chloride. In the present paper, these higher acetylation products have been proved to be $\alpha\gamma$ -C-diacetyl- β -aryl-glutaconic anhydrides (IV).

The α -aceto- β -(4-methoxy-phenyl)-glutaconic anhydride, m.p. 132°C (II) for instance gave, on further acetylation, a product m.p. 108°C, the empirical formulæ ($C_{16}H_{14}O_6$) of which indicated the entry of one more acetyl group. This compound, however, gave a deep violet colouration with ferric chloride, titrated as a strong monobasic acid, and when treated with aniline in benzene solution, gave an aniline salt. These observations exclude the possibility of the product being an O-acetyl-derivative (III) of the C-acetyl-anhydride (II). The anhydride nature of this product, m.p. 108°C is, however, indicated as it gets decomposed even by boiling water

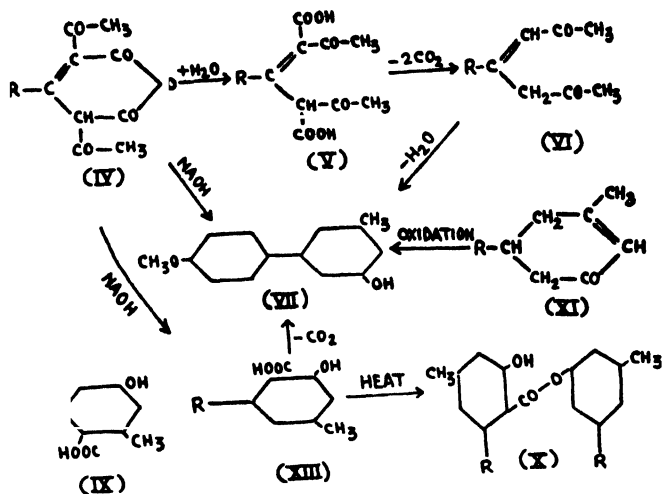
or alcohol. This product, m.p. 108°C , with dilute hydrochloric acid gave the known β -(4-methoxy-phenyl)-propylene (A) and with concentrated hydrochloric acid yielded the lactone, m.p. 112°C (B). In both these reactions, primarily the second acetyl group is removed to regenerate the α -aceto- β -(4-methoxy-phenyl)-glutaconic anhydride (II), which latter, by further action of hydrochloric acid, produced the compounds (A) and (B) in the way indicated in part IV¹. Thus the product, m.p. 108°C , is an acetyl derivative of the α -C-acetyl-anhydride, m.p. 132°C (II), and as O-acetyl is out of question and the tautomeric hydrogen is still free, only the γ -position is available for substitution by the second acetyl group. Hence the product, m.p. 108°C , must be the $\alpha\gamma$ -diaceto- β -(4-methoxy-phenyl) glutaconic anhydride (IV).



(R = 4-methoxy-phenyl)

The $\alpha\gamma$ -C-diacetylation is further supported by the study of the action of caustic alkali on this $\alpha\gamma$ -diaceto- β -(4-methoxy-phenyl)-glutaconic anhydride, m.p. 108°C (IV). This action gave a phenolic body, m.p. 118°C , its empirical formulæ (C₁₄H₁₄O₂) suggesting a loss of two molecules of carbon dioxide, and a phenolic monocarboxylic acid, m.p. 182°C (decomp.). This monocarboxylic acid gave the above phenol, m.p. 118°C , by the loss of carbon dioxide. The phenol, m.p. 118°C , was synthesised by oxidising the known methyl-1-methoxyphenyl-3-cyclohexenon-5⁵, (XI) (Knoevenagel, *Annalen*, 303, 249) by the method of Rabe and Pollock⁸, (Ber., 45, 2926), which fixes its constitution as a hydroxy-diphenyl (VII). In the formation of this phenol, m.p. 118°C , the alkali evidently first opens the anhydride ring of the $\alpha\gamma$ -C-diacetyl-anhydride (IV), and produces the unstable intermediate diketo-diacid (V). This by the further action of alkali loses two molecules of carbon dioxide, and the resulting

diketone (VI) immediately undergoes internal condensation by the elimination of water to produce the hydroxy-diphenyl (VII).

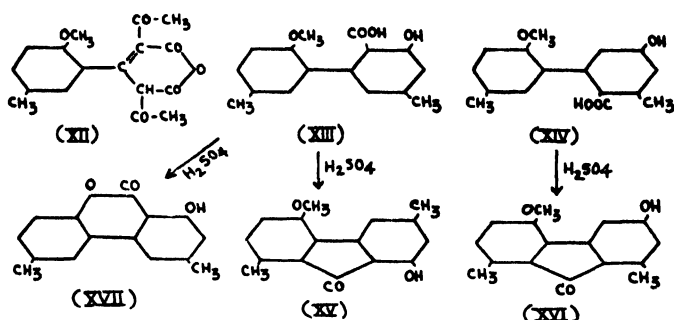


(R = -4methoxy-phenyl)

Now, in the above scheme, the diketo-diacid (V) under the influence of alkali may lose only one molecule of carbon dioxide, followed immediately by the internal condensation. This results in the formation of the phenolic monocarboxylic acid, m.p. $182^\circ C$, which may possess either the ortho-hydroxy (VIII) or the para hydroxy (IX) constitution according to which of the carboxylic groups of the diketo-diacid (V) gets eliminated before the ring closure. The monocarboxylic acid, m.p. 182° , on decomposition at its melting point gave along with the hydroxy diphenyl (VII) an ester (X) of itself with the latter phenol. Out of the ortho-hydroxy-benzoic (salicylic) and para hydroxy benzoic acids, only the former produces such a phenyl-ester (salol) in this manner⁴ (Græbe and Eichengrün, *Annalen*, 269, 324). Hence by this analogy; the phenolic carboxylic acid, m.p. $182^\circ C$, appears to have the constitution (VIII).

The β -(2-methoxy-5-methyl-phenyl)-glutaconic anhydride, on diacetylation by both the methods, gave a similar $\alpha\gamma$ -diaceto- β -(2-methoxy-5-methyl-phenyl)-glutaconic anhydride, m.p. $168^\circ C$ (XII). By the action of caustic alkalis, however, this gave a hydroxy-diphenyl, m.p. $85^\circ C$, similar to (VII), and two hydroxy-diphenyl-monocarboxylic acids melting at $213^\circ C$ (decomp.) and $192^\circ C$ (decomp.). On thermal decomposition, the latter acid gave

only the hydroxy diphenyl, m.p. 85°C , whereas the former acid produced in addition to this hydroxy-diphenyl, its (the acid's) ester with this phenol similar as (X). Hence the acid, m.p. 213°C , has the ortho-hydroxy-structure (XIII) and the other acid, m.p. 192°C , has the para-hydroxy structure (XIV).



The acid, m.p. 213°C (XIII), on treatment with concentrated sulphuric acid, gave the lactone (XVII) and the fluorenone (XV). On treatment with hot alkali followed by dimethyl sulphate, this lactone gives back the acid, m.p. 213°C (XIII)⁵ (*cf.* Gogte, Proc. Ind. Acad. Sci. (A), 1934 1, 48). The other acid, m.p. 192°C (XIV), by treatment with concentrated sulphuric acid gave only the fluorenone (XVI). These fluorenones, due to the depressed reactivity of the carbonyl group do not give ketonic derivatives⁶ (*cf.* Hantzsch, Ber., 23, 2772; Smith, Ber., 24, 4050). Their fluorenone structure is, however, apparent from the method of their formation from the acids (XIII) and (XIV), their dyeing properties, and their colour reactions with concentrated sulphuric acid⁷ (Fitting and Ostermayer, Annalen, 166, 373; Staedel, Ber., 28, 111; Graebe and Aubin, Ber., 20, 847).

CONCLUSION

Further acetylation of the α -aceto- β -aryl-glutaconic anhydrides has been found to produce, not the expected neutral O-acetyl derivatives, but products which have been proved to be $\alpha\gamma$ -diaceto- β -aryl-glutaconic anhydrides. If the titratability and ferric chloride colouration of the glutaconic anhydrides and α -C-monoacetyl derivatives are due to the hydroxy group arising out of the wandering of the mobile hydrogen atom to the neighbouring carbonyl group, it appears strange that on acetylation, the acetyl group should avoid to go, especially in the latter case, to this hydroxy group, and prefer to get attached to the α and γ

carbon atoms. This may be because no such hydroxy group is really formed or if formed is unreactive particularly to acetylation. The titratability and ferric chloride colouration definitely indicates the existence of a very reactive hydrogen atom. Thus the nature of the binding of this hydrogen in the glutaconic anhydride nucleus requires further elucidation.

The reactions described in the present paper incidentally lead to a new and easy method for the preparation of diphenyl derivatives, especially the derivatives of ortho-phenyl-benzoic acids, which are so important, being the source of fluorenones⁷; and phenanthrene derivatives⁸ (Schonberg and Warren, Chem. Ind., 1939, 58, 199).

EXPERIMENTAL

C-diacetylation of β -(4-methoxy-phenyl)-glutaconic anhydride: Formation of $\alpha\gamma$ -diaceto- β -(4-methoxy-phenyl)-glutaconic anhydride (IV):—The β -(4-methoxy-phenyl)-glutaconic acid (25 g.) and fused sodium acetate (50 g.) were powdered together and mixed thoroughly with acetic anhydride (60 c.c.) with shaking. This reaction mixture was heated on a boiling water bath for 10 minutes, the resulting red viscous liquid was then refluxed for 5 minutes and poured in 200 c.c. of water. After keeping for $\frac{1}{2}$ hour, the red aqueous portion was filtered and acidified with conc. hydrochloric acid (60 c.c.). After keeping for 1 hour, the supernatant aqueous portion was decanted off and the resinous red product washed with water. Methyl alcohol was added and the sticky product rubbed continuously with a glass rod when in about $\frac{1}{2}$ hour gradually a granular solid separated. It was filtered, washed with cold methyl alcohol and treated with boiling ethyl acetate (50 c.c.). The insoluble solid was filtered out, and the filtrate concentrated to 20 c.c., when on cooling with ice-water the C-diacetyl anhydride separated. It was recrystallised from ethyl-acetate-petrol mixture in yellowish hexagonal plates, m.p. 108°C. Yield 8 grams. (Found: Eq.=305; C=63.4%; H=4.5%; $C_{14}H_{14}O_4$ requires Eq.=302; C=63.6%; H=4.6%). This C-diacetyl anhydride could also be prepared by acetylating the β -(4-methoxy-phenyl)-glutaconic anhydride by using excess of pyridine acetyl chloride at a temperature of boiling water bath, and pouring in hydrochloric acid; and is purified as above. The compound can also be prepared by acetylating the α -aceto- β -(4-methoxy-phenyl)-glutaconic anhydride (II) by any of the above methods. This C-diacetyl anhydride, m. p. 108°C, gives a violet colouration with ferric chloride in cold alcoholic

solution, and gives an insoluble sodium salt even when treated with normal sodium hydroxide solution. The compound gets decomposed by boiling with water, alcohol, sodium carbonate solution or very dilute sodium hydroxide solution, to give neutral dark coloured resinous products.

Action of hydrochloric acid on the $\alpha\gamma$ -diaceto- β -(4-methoxy-phenyl)-glutaconic anhydride.—The C-diacetyl anhydride, m.p. 180°C , when steam-distilled with dilute hydrochloric acid produces the known β -(4-methoxy-phenyl)-propylene (A)¹; when refluxed with conc. hydrochloric acid for one hour, the C-diacetyl anhydride is converted into a natural oil. This was dissolved in ether, dried, and ether evaporated at room temperature. On keeping the residue in a strong vacuum for eight days, a crystalline solid separated, which was freed from the accompanying oil by porous plate. It crystallised from alcohol in colourless plates, m.p. 112°C and was identical with the known lactone (B)¹.

Action of aniline on $\alpha\gamma$ -diaceto- β -(4-methoxy-phenyl)-glutaconic anhydride.—The C-diacetyl anhydride, m.p. 108°C , was dissolved in benzene, aniline was added and the mixture warmed on a water bath, when its aniline salt instantaneously separated as yellowish light plates. It crystallised from methyl alcohol in hexagonal rods, m.p. 144°C (decomp.). This aniline salt gave a dark blue colouration with ferric chloride. It dissolves in cold sodium carbonate solution and gets immediately decomposed into aniline and the C-diacetyl anhydride m.p. 108°C . (Found: C=66.6%; H=5.1%; $\text{C}_{22}\text{H}_{21}\text{O}_6\text{N}$ requires C=66.8%; H=5.3%).

Action of caustic alkali on the $\alpha\gamma$ -diaceto- β -(4-methoxy-phenyl)-glutaconic anhydride: Formation of diphenyl derivatives.—The C-diacetyl-anhydride (5 g.) was mixed with 10% sodium hydroxide solution (50 c.c.) and the pasty mass heated on a boiling water bath until a clear pale yellow solution was obtained (15 minutes). It was kept overnight at room temperature and acidified. The precipitate which separated after 2 hours was filtered, washed with water and treated with boiling 10% sodium carbonate solution.

The 3-methoxy-4'-methyl-2'-hydroxy-diphenyl (VII).—On cooling and keeping the above sodium carbonate solution for an hour, a solid separated which was filtered, dissolved in methyl alcohol (animal charcoal) and precipitated by water. The hydroxy diphenyl separated as colourless pearly plates which after re-crystallisation from dilute methyl alcohol melt at 118°C . (Found: M.W.—by camphor method—220; C=78.4%; H=6.5%; $\text{C}_{14}\text{H}_{14}\text{O}_2$

requires M.W. = 214; C = 78.5%; H = 6.5%). The *benzoyl derivative*, prepared by the Schotten, Baumann method, crystallised from ethyl alcohol in colourless light silky needles, m.p. 120°C. (Found: C = 78.8%; H = 5.8%; $C_{21}H_{18}O_2$ requires C = 79.0%; H = 5.95%).

The 3-methoxy-4'-methyl-2'-hydroxy-diphenyl-1'-carboxylic acid (VIII):—The sodium carbonate filterates after removing the above hydroxy-diphenyl, were acidified. The diphenyl-carboxylic acid which separated, crystallised from dilute methyl alcohol in light parallelogramic needles, m.p. 182°C. (decomp.). (Found: Eq. = 258; C = 69.9%; H = 5.4%; $C_{18}H_{14}O_4$ requires Eq. = 258; C = 70.0%; H = 5.4%). This acid gives a violet colouration with ferric chloride in cold alcohol. On refluxing with dilute hydrochloric acid for 3 hours, it is converted into the above hydroxy-diphenyl, m.p. 118°C. This acid gave no ester by Fischer and Spier's method but got decarboxylated as above.

Synthesis of 3-methoxy-4'-methyl-2'-hydroxy-diphenyl (VII) by the oxidation of the known methyl-1-methoxyphenyl-3-cyclohexenon-5 (XI)^{2,3}:—The ketone (5 g.) was dissolved in alcohol (150 c.c.) and ferric chloride (15 g.) dissolved in small amount of water was added. The mixture was refluxed for 7 hours and kept overnight at room temperature. Alcohol was distilled off, water added and the whole extracted with ether. The ether solution was washed with water and shaken with 10% sodium hydroxide solution. This sodium hydroxide solution was acidified and kept overnight when the hydroxide-diphenyl, m.p. 118°C. (VII) separated. Yield, 0.5 gram.

Thermal decomposition of the 3-methoxy-4'-methyl-2'-hydroxy-diphenyl-1'-carboxylic acid (VIII):—The diphenyl-carboxylic acid, m.p. 182°C (1 g.) was decomposed in a hard glass tube at 200°C temperature and 40 m.m. pressure, until gas evolution ceased. The residue was dissolved in ether, washed with sodium carbonate solution, water, and the ether allowed to evaporate at room temperature. The resulting solid was dissolved in boiling methyl alcohol (30 c.c.) filtered, and the solution concentrated to 10–15 c.c. On cooling and scratching, a substance separated which crystallised from methyl alcohol in colourless rhombohedrons m.p. 119°C. Yield, 0.4 gram. (Found: C = 76.4%; H = 5.5%; $C_{20}H_{16}O_2$ requires C = 76.65%; H = 5.7%). This compound gives a green colouration with ferric chloride in cold alcohol. On refluxing with 10% sodium hydroxide, it dissolves and gets converted into the hydroxy-diphenyl, m.p. 118°C (VII), and the hydroxy-diphenyl-carboxylic acid, m.p. 182°C (VIII), and hence

is their ester (X). The methyl alcoholic filterates after removing this ester, were diluted with water, when the hydroxy-diphenyl, m.p. 118°C (VII) crystallised out. Yield, 0.3 gram,

C-diacetylation of β -(2-methoxy-5-methyl-phenyl)-glutaconic anhydride: Formation of $\alpha\gamma$ -diaceto- β -(2-methoxy-5-methyl-phenyl)-glutaconic anhydride (XII):—The β -(2-methoxy-5-methyl-phenyl)-glutaconic acid (50 g.) and fused sodium acetate (100 g.) were finely powdered together and refluxed with acetic anhydride (150 c.c.) for about 20 minutes; when a precipitate began to separate and in a short time, the whole solidified. Water (500 c.c.) was added and after about an hour, the clear red solution was filtered to remove black resinous impurities, and acidified by hydrochloric acid (60 c.c.). After keeping for an hour at room temperature, the granular precipitate was filtered, washed with water, dried and twice crystallised from ethyl acetate. The C-diacetyl anhydride separated in yellowish parallelogramic plates, m.p. 168°C. Yield, 35 grams. (Found: Eq.=313; C=64.4%; H=5.0%; $C_{17}H_{16}O_6$ requires, Eq.=316; C=64.5%; H=5.0%). This compound gives a violet colouration with ferric chloride in cold alcohol, and behaves like the compound (IV) in regard to other methods of preparation and action towards water alcohol, etc.

Action of hydrochloric acid:—The C-diacetyl anhydride was refluxed with conc. hydrochloric acid for 3 hours, the resulting yellow oil extracted with ether, washed with sodium carbonate solution, water, and ether removed. The residual heavy viscous oil was refluxed with 5% sodium hydroxide solution, the undissolved oil removed with ether, and the alkali solution acidified. The resulting oily acid was dissolved in benzene, the solution dried, and precipitated by petroleum ether, when on scratching and keeping, an acid separated in colourless needles, m.p. 101°C, and was identified as the 2-methoxy-5-methyl- β -acetonyl-cinnamic acid.¹

Action of caustic alkali on the $\alpha\gamma$ -diaceto- β -(2-methoxy-5-methyl-phenyl)-glutaconic-anhydride (XII): Formation of diphenyl-derivatives:—The C-acetyl-anhydride (XII) (20 g.) was dissolved in 10% sodium hydroxide solution (400 c.c.) and the deep orange solution refluxed till it turned pale yellow (15 minutes). It was filtered and acidified and the sticky solid which separated on keeping for 4 hours was filtered, washed with water, and treated with boiling sodium carbonate solution.

1-Methoxy-4:4'-dimethyl-2'-hydroxy-diphenyl (cf. VII):—The oily substance insoluble in sodium carbonate in above was extracted

with ether, ether removed, the residue dissolved in 10% sodium hydroxide solution and 50% sodium hydroxide solution was added, when a sodium salt separated as colourless silky needles. This was filtered and decomposed by acids and the resulting hydroxy-diphenyl was extracted with ether, dried, ether removed and crystallised from petroleum ether in colourless prismatic needles, m.p. 85°C. Yield, 2.5 grams. (Found: M. W.—by Beckmann's method—225; C=78.8%; H=7.0%; $C_{18}H_{16}O_2$ requires, M. W.=228; C=78.9%; H=7.0%). The *acetyl derivative* prepared by acetic anhydride and sodium acetate, is a heavy thick oil, b.p. 181-185°C/6 m.m. (Found: C=75.2%; H=6.5%; $C_{17}H_{14}O_3$ requires, C=75.5%; H=6.7%).

1-Methoxy-4 : 4'-dimethyl-2'-hydroxy-diphenyl-1'-carboxylic acid (XIII):—The sodium carbonate solution after removing the above hydroxy-diphenyl, m.p. 85°C, was acidified which gave a mixture of acids. Yield, 14 grams. This whole was dissolved in boiling methyl alcohol (200 c.c.) filtered, and the solution concentrated to 100 c.c. when on cooling, the 1'-carboxylic acid separated in colourless light plates. Recrystallised from ethyl acetate, m.p. 213°C (decomp). Yield, 6 grams. (Found: Eq.=273; C=70.5%; H=5.8%; $C_{18}H_{16}O_4$ requires, Eq.=272; C=70.6%; H=5.9%). This acid gives a violet colouration with ferric chloride in cold alcohol. It is unaffected by boiling hydrochloric acid and could not be esterified by Fischer Spier's method.⁹ (cf. V. Meyer, Ber., 1895, 28, 1254). The *acetyl derivative* prepared by acetic anhydride and sodium acetate, crystallised from dilute methyl alcohol in colourless transparent needles, m.p. 161°C. (Found: C=68.6%; H=5.6%; $C_{18}H_{14}O_5$ requires, C=68.8%; H=5.7%). *Thermal decomposition* of this acid at 200°C/35 m.m. gave a sticky product from which, on rubbing with methyl alcohol, its (the acid's) ester (as X) with the hydroxy-diphenyl, m.p. 85°C, separated as a precipitate. It was filtered, washed with hot sodium carbonate solution and crystallised from ethyl acetate in colourless rectangular plates, m.p. 127°C. It gives a green colouration with ferric chloride, and gets decomposed by caustic alkalis in the 1'-carboxylic acid, m.p. 213°C, and the hydroxy-diphenyl, m.p. 85°C. (Found: C=76.9%; H=6.0%; $C_{21}H_{20}O_5$ requires, C=77.2%; H=6.2%). The methyl alcoholic filterates after removing this phenyl ester, on concentration produced the hydroxy-diphenyl, m.p. 85°C, which was separated and purified as described before.

1-Methoxy-4 : 4'-dimethyl-2'-hydroxy-diphenyl-5'-carboxylic acid (XIV):—From the methyl alcoholic filterates obtained after

removing the above 1'-carboxylic acid (XIII), alcohol was distilled off, the residue dissolved in sodium carbonate solution, filtered and acidified. The oily mass which separated, solidified by scratching and keeping, was filtered and repeatedly extracted by boiling water (600 c.c.). The solid which crystallised from the aqueous filtrate was refluxed with 20 % sodium hydroxide solution (2 hours) and acidified. The precipitate was dissolved in cold sodium carbonate solution, filtered, washed with ether and acidified. The diphenyl-5'-carboxylic acid which separated was crystallised from 25 % methyl alcohol in colourless rectangular plates, m.p. 192°C. (decomp.). Yield, 2.5 g. (Found : Eq.=272 ; C=70.4 %; H=5.8 %; $C_{18}H_{16}O_4$ requires, Eq.=272; C=70.6 %; H=5.9 %). This 5'-carboxylic acid gives deep violet colouration with ferric chloride in cold alcohol. It very easily loses carbon dioxide by refluxing with mineral acids or by decomposing it at its melting point under reduced pressure, to produce the hydroxy-diphenyl, m.p. 85°C. Hence it could not be esterified by Fischer and Spier's method.

The residue insoluble in boiling water in above, crystallised from 75 % methyl alcohol in parallelogramic plates, m.p. 180-200°C. It gave a violet colouration with ferric chloride and showed an equivalent below 190.

Action of sulphuric acid on 1-methoxy-4 : 4'-dimethyl-2'-hydroxy diphenyl-1'-carboxylic acid (XIII) and 5' carboxylic acid (XIV) : Formation of fluorenone derivatives:—The 1'-carboxylic acid (XIII), m.p. 213°C, was dissolved in conc. sulphuric acid, and the dark green solution after keeping at 70°C for 1 hour was poured in water. The yellow precipitate was filtered, washed with boiling sodium carbonate solution and refluxed with 25 % sodium hydroxide solution for 2 hours. On cooling, the insoluble yellow solid was filtered out, and the alkali filtrates acidified.

The 1 : 1'-lactone of 4 : 4'-dimethyl-1 : 2'-dihydroxy-diphenyl-1'-carboxylic acid (XVII):—This separated on boiling the above acidified solution as a faint yellow precipitate, which crystallised from ethyl acetate in colourless rectangular plates, m.p. 194°C. (Found : C=74.9 %; H=5.0 %; $C_{18}H_{16}O_3$ requires, C=75.0 %; H=5.0 %). This lactone dissolved when refluxed with 20 % sodium hydroxide solution, and when this alkali solution is gradually treated with excess of dimethyl sulphate at 100°C, and acidified, the original 1'-carboxylic acid, m.p. 213°C, (XIII) could be obtained from the resulting mixed acids by crystallising from methyl alcohol. This lactone, m.p. 194°C, gives a blue colouration with ferric chloride in cold alcohol. The *acetyl derivative* prepared by acetic

anhydride and sodium acetate, crystallised from methyl alcohol in colourless flat needles, m.p. 163°C . (Found: $\text{C}=72.1$; $\text{H}=4.8\%$; $\text{C}_{11}\text{H}_{14}\text{O}_4$ requires, $\text{C}=72.3\%$; $\text{H}=5.0\%$).

The 1:3'-dimethyl-4-methoxy-1'-hydroxy-fluorenone (XV):— The fluorenone as the yellow solid insoluble in 25% sodium hydroxide, was washed with water, dried and crystallised from ethyl acetate in yellow silky needles, m.p. 168°C . (Found: $\text{C}=75.5\%$; $\text{H}=5.4\%$; $\text{C}_{16}\text{H}_{14}\text{O}_3$ requires $\text{C}=75.6\%$; $\text{H}=5.5\%$). This fluorenone gives a strong yellow alcoholic solution having dyeing properties. It dissolves in cold sulphuric acid giving dark green solution. It gives a brown colouration with ferric chloride in cold alcohol. The *acetyl derivative* prepared by acetic anhydride and sodium acetate, crystallised from acetic acid in yellow short needles, m.p. 191°C . (Found: $\text{C}=72.7\%$; $\text{H}=5.2\%$; $\text{C}_{18}\text{H}_{16}\text{O}_4$ requires, $\text{C}=73.0\%$; $\text{H}=5.4\%$).

1:1'-Dimethyl-4-methoxy-3'-hydroxy-fluorenone (XVI):— The 5'-carboxylic acid, m.p. 192°C (XIV) was dissolved in cold sulphuric acid, the dark green solution kept overnight at room temperature and poured in water. The yellow precipitate was filtered, washed with hot sodium carbonate solution, and treated with 10% sodium hydroxide solution when it all dissolved giving an orange red solution. This was filtered, acidified, and the precipitated fluorenone crystallised from boiling alcohol in yellow microscopic needles, m.p. 264°C . (Found: $\text{C}=75.3\%$; $\text{H}=5.3\%$; $\text{C}_{16}\text{H}_{14}\text{O}_3$ requires, $\text{C}=75.6\%$; $\text{H}=5.5\%$). The alcoholic and alkali solutions of this fluorenone have strongly dyeing properties. The compound gives a brown colouration with ferric chloride in cold alcohol. The *acetyl derivative* prepared by acetic anhydride and sodium acetate, crystallised from alcohol in yellow silky needles, m.p. 172°C . (Found: $\text{C}=72.8\%$; $\text{H}=5.2\%$; $\text{C}_{18}\text{H}_{16}\text{O}_4$ requires, $\text{C}=73.0\%$; $\text{H}=5.4\%$).

$\alpha\gamma$ -C-diacetylation of β -(4-methoxy-3-methyl-phenyl)-glutaconic anhydride (as IV):— The mixture of β -(4-methoxy-3-methyl-phenyl)-glutaconic acid (20 g.), fused sodium acetate (45 g.) and acetic anhydride (50 c.c.) was heated on a boiling water bath for 10 minutes, then refluxed for 15 minutes and poured in water (300 c.c.). After keeping for two hours, the red solution was filtered and acidified. After four hours the aqueous portion was decanted off and the precipitate was rubbed with cold methyl alcohol and crystallised from ethyl acetate. The C-diacetyl anhydride separated in yellow diamond shaped piramids, m.p. 158°C . (decomp.). This compound gives violet colouration with

ferric chloride, and dissolves in cold dilute alkalis. (Found: C=64.3%; H=4.9%; $C_{17}H_{16}O_6$ requires, C=64.5%; H=5.0%).

4:4'-Dimethyl-3-methoxy-2'-hydroxy-diphenyl (as VII) and 4:4'-dimethyl-3-methoxy-2'-hydroxy-diphenyl-1'-carboxylic acid (as VIII):—Both these compounds are obtained by the action of 10% sodium hydroxide solution on the above C-diacetyl anhydride, m.p. 158°C, and are separated by means of sodium carbonate solution. The hydroxy-diphenyl crystallised from petroleum ether in colourless microscopic needles, m.p. 69°C. (Found: C=78.6%; H=6.8%; $C_{18}H_{16}O_2$ requires, C=78.9%; H=7.0%). The 1'-carboxylic acid was refluxed with water and crystallised from dilute methyl alcohol in parallelogramic plates, m.p. 172°C. (decomp.). (Found: Eq.=270; C=70.3%; H=5.7%; $C_{18}H_{16}O_4$ requires, Eq.=273; C=70.6%; H=5.9%). This 1'-carboxylic acid gives the hydroxy-diphenyl, m.p. 69°C, on decarboxylation by mineral acids or heat, as also in latter case its ester, m.p. 108°C, with the hydroxy-diphenyl.

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DIELECTRIC PROPERTIES OF GLYCERIDES

PART II

By

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In part I of this series (J., Bom. Univ., 1938, 93), the dielectric constants of tristearin were determined at different temperatures. In this communication the dielectric properties of α monostearin and α monomyristin have been studied on analogous lines.

The polymorphic properties of mono-glycerides have been noticed since long. Rewadikar and Watson (J. Ind. Inst. Sc., Vol. 13A, 1928, 128) first carried out a systematic investigation of these substances by studying the melting points of the chilled melts and crystalline samples of highly purified glycerides under different conditions. Their conclusions can be summarised in the following way:—

(a) The mono-glycerides of the four higher acids (lauric acid to stearic acid) exhibit two definite melting points corresponding to two polymorphic forms which they term α and β . The rate of conversion of the unstable α form into the stable β form increases with decrease in molecular weight and is almost instantaneous in monolaurin while in the case of monostearin the unstable α form does not change into the β form on keeping just above its melting point for 45 minutes. The corresponding change, in the case of monomyristin is quite rapid above its melting point.

(b) The solidification points of the fused glycerides always lie below the melting point of the β form indicating that the transformation of α form into β form is not complete.

Maikin and Shurbagy (J. Chem. Soc., 1936, 1628.) have confirmed these results and in addition have established the existence of a third form.

EXPERIMENTAL.

The monoglycerides were prepared by the method of Malkin and Shurbagy (loc. cit.). They were crystallised several times till perfectly pure. The method of measurement was the same as described in part I. (loc. cit.). The experimental condenser used was however of a different type. It consisted of three silver plated brass strips (fig. I). The outer plates were semi-cylindrical

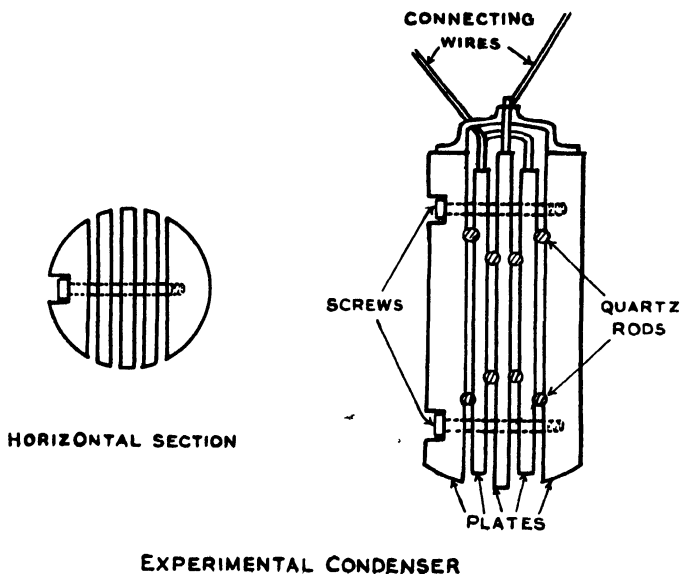


Fig. 1

and the central plate was rectangular. The central plate was insulated from the outer plates by quartz rods put into small grooves cut in the plates. The outer plates were earthed and were held in place by bolts. The condenser thus formed was introduced into a pyrex test tube. The arrangement was quite rigid and the air capacity did not change appreciably with temperature. The cylindrical plates, being of solid brass, ensured uniformity of temperature. The capacity was $36.2 \mu\text{F}$ and 15 c.c. of the liquid were required to cover the plates completely. Benzene was used as a standard substance for calibration.

Both the glycerides showed absorption. This is being further studied. The following tables give the results. D. C. indicates dielectric constant.

MONOMYRISTIN

A sample of pure monomyristin was kindly supplied by Professor R. S. Rewadikar of Madhav College, Ujjain. Most of the experiments were carried out with this specimen. The substance melted at 70.5° .

Experiment I

Monomyristin was heated to 85° and the liquid was introduced into the condenser. It was then gradually allowed to cool. Reading for dielectric constants were taken at intervals.

TABLE I

Frequency 1000 kc/s.		Frequency 4400 kc/s.	
Temp.	D. C.	Temp.	D. C.
73.8	5.88	84.0	6.02
72.8	5.89	79.1	6.14
71.1	5.92	76.7	6.20
69.9	5.95	74.2	6.23
68.7	5.98	71.0	6.32
67.8	6.02	69.0	6.36
65.8	6.05	63.3	6.39
64.6	6.06	61.8	6.42
63.7	6.09	59.5	6.45
62.4	6.13	58.2	6.48
61.3	6.16	Solidifies at 57.7°	
58.1	6.11	56.5	3.24
Solidifies at 57.7°		55.4	3.09
57.5	3.44	52.7	2.96
56.3	3.30	48.8	2.81
53.7	3.17	46.6	2.68
50.7	2.81	42.1	2.61
45.8	2.54	38.6	2.54
41.2	2.50	32.5	2.49
36.4	2.48	27.7	2.46
31.5	2.47	23.5	2.46
25.8	2.43		

Experiment II

The substance was allowed to remain at the room temperature for about four days after melting and then gradually heated when the dielectric constants were measured at intervals. The substance melted at 70.5° .

TABLE II

Frequency 1000 kc/s.		Frequency 4400 kc/s.	
Temp.	D. C.	Temp.	D. C.
24.1	2.29	23.5	2.31
26.3	2.31	27.3	2.32
29.2	2.32	29.6	2.34
32.1	2.36	31.2	2.36
36.5	2.40	35.0	2.39
39.2	2.43	38.7	2.43
43.4	2.48	40.1	2.47
45.8	2.51	43.5	2.50
48.4	2.54	45.9	2.53
52.1	2.46	49.4	2.56
54.4	2.59	52.4	2.59
56.5	2.67	58.6	2.77
59.1	2.82	61.2	2.86
61.8	2.92	63.5	3.01
64.4	3.41	64.8	3.38
66.7	3.81	66.7	3.87
69.11	3.89	68.7	3.92
Melts at 70.5°		Melts at 70.5°	
70.9	5.95	70.8	6.31
72.6	5.90	73.8	6.27
74.5	5.87	75.2	6.22
76.2	5.79		

Experiment III

The substance was heated to 80° and suddenly cooled in a mixture of ice and salt. It was then gradually heated when dielectric constants were determined at different temperatures. The substance melted at 67.5° .

TABLE III

Frequency 1000 kc/s.		Frequency 4400 kc/s.	
Temp.	D. C.	Temp.	D. C.
18.2	4.18	11.2	6.70
22.5	4.23	16.7	7.29
25.5	4.38	19.5	7.59
26.7	4.38	23.5	7.90
29.5	3.09	26.1	8.17
31.7	2.95	29.9	8.70
33.8	2.92	31.4	3.72
35.3	2.89	34.2	3.78
40.4	2.86	41.3	3.86
45.8	2.86	45.5	3.89
47.6	2.89	47.6	3.90
49.2	2.93	50.7	3.96
51.6	2.94	55.2	4.09
55.5	2.97	58.6	4.34
57.1	3.03	62.3	4.69
59.4	3.13	65.5	5.02
64.6	3.52	66.4	5.33
66.4	3.87	Melts at 67.3°	
67.1	4.24		
Melts at 67.3°		69.0	6.35
		69.5	6.31
69.5	5.93	71.4	6.27
73.7	5.86	74.8	6.10

The same experiment was repeated when the substance was kept in a mixture of ice and salt for a long time. In this case the break was observed at 39.5°

TABLE IV

Frequency 1000 kc/s.

Frequency 4400 kc/s.

Temp.	D. C.	Temp.	D. C.
18.0	5.12	5.0	6.16
21.8	~~5.12~~ 5.98	7.0	6.25
23.5	6.50	12.7	6.70
25.9	7.19	15.2	7.01
29.3	8.04	17.3	7.31
32.5	8.21	21.5	7.94
35.3	8.37	25.9	8.35
38.2	8.58	28.7	8.57
40.1*	3.09	30.4	8.70
43.0	2.90	34.9	8.86
46.0	2.84	38.7	8.98
48.8	2.84	40.2*	3.72
51.4	2.85	42.6	3.72
53.6	2.85	45.2	3.73
57.3	2.88	48.4	3.74
59.3	2.94	52.1	3.78
62.3	3.00	55.2	3.96
63.9	3.26	57.7	4.21
65.7	3.58	62.2	4.77
67.2	3.79	64.5	5.01
Melts at 67.3°		66.9	5.40
69.5	5.98	Melts at 67.3°	
71.3	5.90	68.7	6.34
73.7	5.86	70.6	6.29
75.9	5.84	73.7	6.26

Experiment IV

The substance was heated to 80° and suddenly cooled in a mixture of solid carbon dioxide and toluene. It was then gradually heated when readings for dielectric constants were taken. The substance melts 67.5° . A break was obtained at 39.5° .

TABLE V

Frequency 1000 kc/s.		Frequency 4400 kc/s.	
Temp.	D. C.	Temp.	D. C.
5.0	3.92	7.5	6.28
7.5	3.99	11.6	6.38
10.7	4.25	17.6	6.65
13.3	4.69	20.2	6.91
15.6	4.97	22.9	7.15
18.7	5.56	25.7	7.49
21.6	5.82	29.7	7.66
24.8	6.33	33.6	7.76
29.3	6.82	35.5	7.77
33.4	7.15	38.2	7.78
35.2	7.32	40.1*	3.69
38.5	7.54	42.5	3.74
40.2	2.91	45.9	3.79
42.2	2.90	50.1	3.85
45.3	2.90	52.4	3.88
47.9	2.90	57.7	3.91
51.5	2.90	58.6	4.26
53.2	2.92	60.0	4.55
56.0	2.94	63.3	4.65
59.9	3.12	65.6	4.78
63.1	3.34	66.9	4.89
66.0	3.84	Melts at 67.5°	
Melts at 67.5°		68.7	6.35
68.2	6.02	70.6	6.30
71.8	5.95	72.8	6.26
75.9	5.84	71.1	6.20

MONOSTEARIN.

Experiment I

The substance was heated to 90° and introduced into the cell at the same temperature and was gradually allowed to cool. Readings for dielectric constants were taken at intervals. Monostearin solidified at 70.8° .

TABLE VI.

Frequency 1000 kc/s.		Frequency 5700 kc/s.	
Temp.	D. C.	Temp.	D. C.
87.7	4.30	88.0	4.52
82.3	4.34	85.0	4.53
79.7	4.35	81.3	4.55
75.0	4.37	79.4	4.58
71.2	4.39	74.5	4.64
Solidified at 70.8°		72.2	4.66
70.5	4.69	Solidified at 70.8°	
69.4	4.75	70.5	5.12
67.0	4.82	69.5	5.18
65.5	4.85	68.8	5.20
62.4	4.86	61.6	5.21
58.5	4.85	58.5	5.22
51.7	4.85	54.1	5.27
47.4	4.84	52.7	5.32
46.0	4.83	50.4	5.32
44.0	4.69	45.8	5.12
43.0	4.52	44.5	4.86
42.5	4.45	44.0	4.80
39.1	4.42	43.0	4.74
35.6	4.36	42.0	4.70
31.5	4.21	39.9	4.62
30.6	4.18	37.7	4.45
28.6	4.11	35.4	4.30
25.5	3.96	33.0	4.12
23.8	3.91	31.4	3.88
		26.1	3.40
		25.2	3.35

Experiment II

The substance was heated to 90° and suddenly cooled in a mixture of ice and salt where it was kept for two hours. It was then gradually heated and readings for dielectric constants were taken. It melted at 74.5° .

TABLE VII.

Frequency 1000 kc/s.		Frequency 5700 kc/s.	
Temp.	D. C.	Temp.	D. C.
16.5	3.92	14.8	3.28
18.0	4.01	17.5	3.38
20.9	4.09	20.0	3.51
24.2	4.29	22.3	3.84
27.0	4.51	25.7	4.11
30.8	4.92	28.0	4.69
37.4	4.94	29.6	4.94
39.4	4.96	31.2	5.00
43.4	4.98	35.4	5.20
46.4	5.01	41.3	5.28
48.2	5.15	44.5	5.39
50.0	5.36	45.6	5.45
53.1	5.37	47.8	5.55
55.0	5.37	49.0	5.82
61.9	5.38	50.2	5.88
66.0	5.35	51.3	5.87
70.2	5.33	56.0	5.89
72.4	5.32	64.0	5.91
74.0	5.16	68.5	5.88
Melts at 74.5°		72.0	5.83
75.1	4.38	73.9	5.81
76.8	3.37	Melts at 74.5°	
		75.0	4.65
		77.5	4.61

Experiment III

Monostearin (in the previous experiment) was maintained at the room temperature for 15 hours and then gradually heated when readings for dielectric constants were taken. The substance melted at 74.5° .

TABLE VIII.

Frequency 5700 kc/s.

Temp.	D. C.	Temp.	D. C.
23.5	2.86	57.5	4.21
25.6	2.97	59.1	4.28
28.3	3.08	60.7	4.34
30.5	3.13	62.8	4.36
33.7	3.20	63.3	4.40
36.3	3.28	65.8	4.41
39.6	3.47	69.9	4.44
42.5	3.55	71.0	4.49
44.8	3.62	72.5	4.57
46.4	3.67	73.8	4.59
48.8	3.68	Melts at 74.5°	
51.2	3.79	75.0	4.60
52.7	3.98	77.5	4.58
56.2	4.14	79.4	4.56

Experiment IV

The substance was kept at room temperature for 6 days and then gradually heated when readings for dielectric constants were taken. Most of the substance melted at 74.5° and there was a small break at 81.1° showing that there was a partial transformation into the stable β form.

TABLE IX

Frequency 1000 kc/s.

Temp.	D. C.	Temp.	D. C.
23.5	2.80	69.8	3.21
24.5	2.82	71.1	3.24
27.6	2.84	72.5	3.36
30.0	2.86	73.8	3.45
33.5	2.90	Melts at 74.5°	
39.6	2.93	74.9	3.81
42.5	2.95	76.2	3.83
47.4	2.98	77.2	3.86
52.4	3.00	79.1	3.95
54.0	3.01	Break at 81.1°	
58.3	3.02	81.9	4.36
62.8	3.07	84.5	4.32
65.5	3.12	88.6	4.29

Experiment V

The substance was kept at the room temperature for a month when most of it was transformed into the stable form. It was then gradually heated when readings for dielectric constants were taken at intervals. There was a distinct break at 74.5° and again at 81.1° at which temperature the substance melted.

TABLE X
Frequency 5700 kc/s.

Temp.	D.C.	Temp.	D.C.
23.6	2.37	69.9	2.69
27.7	2.39	72.4	2.73
30.3	2.40	73.4	2.88
36.5	2.43	Break at 74.5°	
39.7	2.45	74.9	4.01
44.0	2.48	76.0	4.02
47.8	2.51	79.1	4.03
53.1	2.55	melts at 81.1°	
59.8	2.58	81.4	4.56
63.6	2.60	84.6	4.54
66.0	2.64	87.2	4.52

DISCUSSION OF THE RESULTS

The melting points of the different polymorphic forms of the two monoglycerides is given below using the terminology of Malkin and Shurbagy (loc. cit.).

TABLE XI

α -monoglycerides	α form	β' form	β form
α -monomyristin	56°	67.5°	70.5°
α -monostearin	74°	79°	81.5°

MONOMYRISTIN

Table I gives the dielectric constants of a mixture of α and β form. The D. C. is 2.43 at 25°. This is considerably smaller than the D. C. for the liquid (6.2 at 58°). On keeping this substance for four days it was found that the D. C. fell down further to 2.3 at 25°.

the transformation taking place at room-temperature from α form into the stable β form. This is indicated by the fact that it melts at 70.5° . Table II (curve II, Fig. 2) therefore gives the variation of D. C. of the β form with temperature.

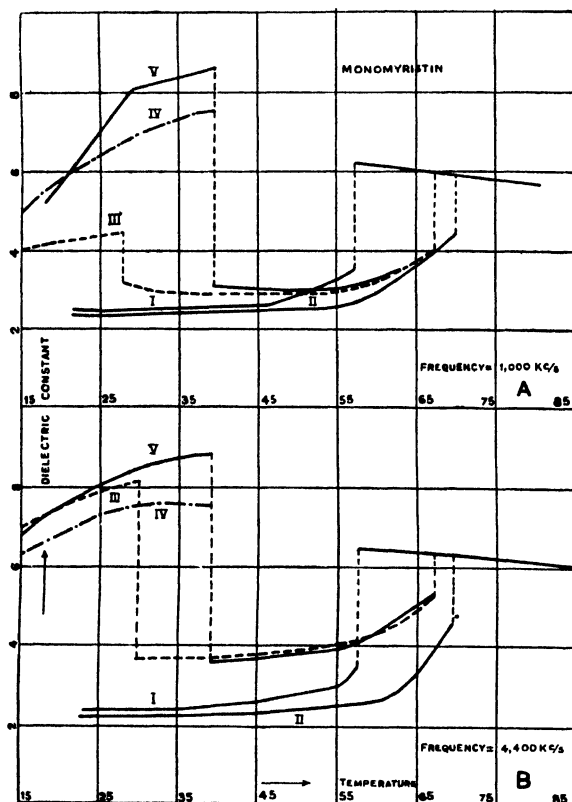


Fig. 2

In experiment III the substance was chilled in a freezing mixture, a solid having the nature of a glass being formed. This solid has a high D. C. (4.38 at 25) much higher than the D. C. of the β form, indicating a condition similar to a supercooled liquid. On heating slowly to 27° a sudden drop in D. C. from 4.38 to 2.95 (at 32) is observed. On further heating it melts at 67.5° (the melting point of the α form). The temperature 27° thus appears to be the transition temperature of the glass changing into α form. A similar arrest in the cooling curve of the glyceride has been observed by Malkin at 24.

If however the melted liquid is allowed to stay for a couple of hours, in the freezing mixture the transformation does not take place at 27 but at 39 (curve IV). The same can be achieved by chilling the melted glyceride in a mixture of toluene and solid carbon di-oxide. This shift in the transition temperature is due to complete transformation into the glass, since the D. C. is nearer to the value for the liquid. Another interesting point is that the glycerides show a gradual rise in D. C. just before the melting point is approached. This may be due to partial melting. All the polymorphs have a higher D. C. at increased frequency.

MONOSTEARIN.

Curve I (Fig. III) shows the variation of the D. C. with temperature when the melted glyceride was gradually cooled.

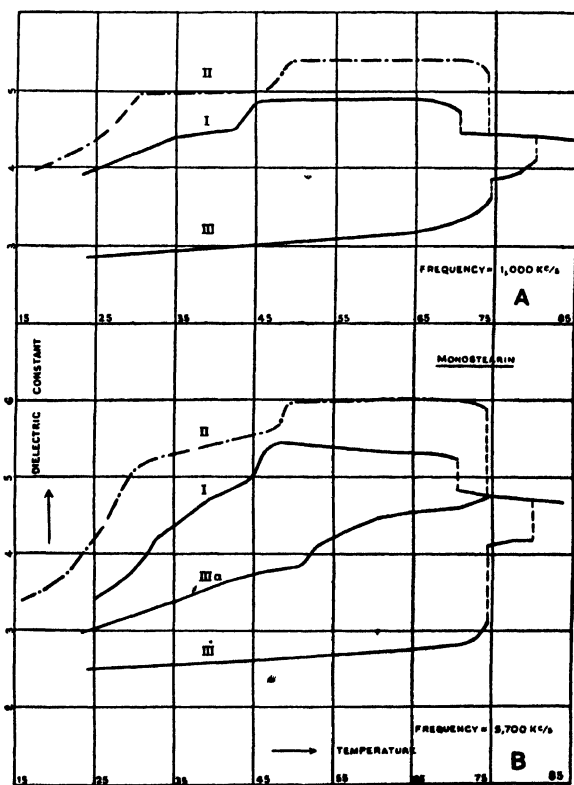


Fig. 3

Unlike monomyristin the D. C. of the solid which melts at 70.8 , is higher than that of the liquid. The D. C. remains practically constant till the temperature 47° is reached when it rapidly begins to fall. The α form is obtained on chilling the melted glyceride in a freezing mixture. Curve II shows the nature of the D. C. Two distinct breaks are observed one at 47 and the other at 30 . It is to be noted that the α form above 47 has the highest D. C. This indicates freedom for molecular rotation. The corresponding arrests obtained by Malkin are 47.5 and 42 . The results could be reproduced several times.

The α form gradually changes into the β form and even after a number of days the transformation is only partial. Curve III-A shows the behaviour of the substance after being allowed to remain at room temperature for fifteen hours. The whole of the substance melted at 74.5° indicating that there was no transformation into the β form. Curve III is obtained after a duration of 6 days. In this case the substance melts partially at 74.5° and completely at 81.1° . Hence two breaks are observed one at 81.1 and the other 74.5° . The melted substance was then allowed to remain at room temperature for a month. In this case after a break at 74.5° the substance melted at 81.1° (curve III) which shows that even then the transformation was not complete. The D. C. in this form is much less than in any other form. The stable form has thus the least D. C. The β' form which melts at 79° could not be obtained. In the case of both the glycerides the D. C. increased with frequency. The following table gives the D. C. of the various forms obtained at the temperatures indicated in brackets.

TABLE XII.

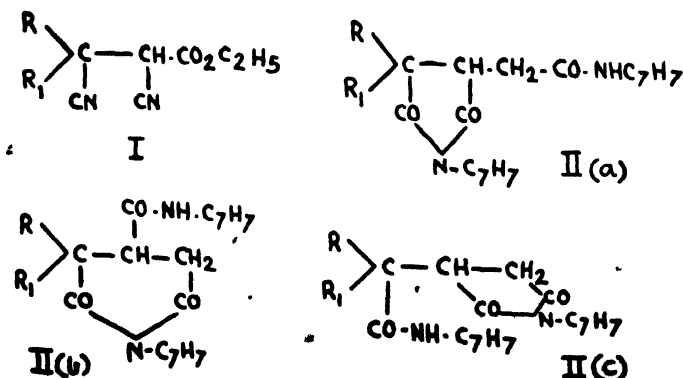
α monoglyceride	α form	β' form	β form
α monomyristin	$8.58 (38.2^{\circ})$	$2.86 (40^{\circ})$	$2.41 (40^{\circ})$
α monostearin	$4.96 (40^{\circ})$	...	$2.40 (40^{\circ})$

THE SYNTHESIS OF α - α -DIMETHYLTRICARBALLYLIC AND 1-CARBOXY-CYCLOPENTANE-1- α -SUCCINIC AND 1-CARBOXY-3-METHYLCYCLOPENTANE-1- α -SUCCINIC ACIDS

By

R. D. DESAI AND G. S. SAHARIYA.

Clemons and Welch* tried to synthesise α - α -dimethyltricarballic acid by the action of ethylbromacetate on the sodium derivative of the dicyanoester obtained by the action of ethyl sodiocyanoacetate on acetone-cyanohydrin (I, where $R=R_1=Me.$), but the yield was very poor (hardly 5 percent.). In a previous publication Desai, Hunter and Sahariya† showed that this reaction went smoothly if $R R_1 =$ alkylcyclohexane ring. Extending this reaction further to cases where $R R_1 =$ cyclopentane or methylcyclopentane rings, we find that excellent yields of tricarballic acids are obtained. Even in the case of acetone, we have improved the yield to 45%. Thus this method constitutes a very general method for the preparation of α - α -disubstituted tricarballic acids. The acids are best characterised by their tolyltoluidides having the general formula IIa or IIb or IIc. When this work was almost over, there appeared a paper by Chatterji‡ nearly two years ago, but as our observations differ in certain respects, we have thought it advisable to publish our data on α - α -dimethyltricarballic and 1-Carboxy-Cyclopentane-1- α -succinic acids.



* Clemons and Welch., J.C.S. (1928), 2621.

† Desai, Hunter and Sahariya, *Ibid* (1939), 84.

‡ Chatterji, Jour., Ind. Chem. Soc. (1937), 14, 127.

EXPERIMENTAL

A suspension of ethylsodiocynoacetate ($\text{Na}=4.2\text{g}$; cyanoacetate= 24g ; ethylalcohol= 40cc) was added to a solution cyclopentanone cyanohydrin (21g .) in absolute alcohol (25c.c.) with constant stirring and cooling. After allowing the mixture to stand at the ordinary temperature for 48 hours, ethylbromacetate (32g .) was added "in Situ," in three lots, cooled, kept at the ordinary temperature for two days, and heated under reflux till the mixture was neutral. After distilling off as much of alcohol as possible, the oil precipitated on diluting the residue with water was extracted with ether, dried, and distilled, under reduced pressure. Three fractions were collected: (1) b.p. $90-120^\circ/4\text{mn}$. (2) b.p. $120-165^\circ/4\text{mn}$. (3) b.p. $185-187^\circ/4\text{mn}$. The first fraction was rejected, while the second fraction was treated again with ethyl bromacetate in presence of sodium ethoxide. Total yield of *ethyl 1-cyanocyclopentane-1- α -cyanosuccinate* boiling at $185-187^\circ/4\text{mn}$ was 45 per cent. (Found: C, 61.4; H, 6.9; $\text{C}_{15}\text{H}_{20}\text{O}_4\text{N}_2$ requires C, 61.6; H, 6.8 per cent).

Hydrolysis of the ester to 1-Carboxy-Cyclopentane-1-succinic acid.

The ester (15g .) which was dissolved in concentrated H_2SO_4 (30c.c.) and kept over-night was diluted with water (40c.c.) and the mixture heated under reflux on sand bath for 20 hours. The cooled mixture was diluted with water, saturated with ammonium sulphate, extracted with ether, and purified through sodium carbonate. The crude acid which melted at $130-136^\circ$ was refluxed with benzene, and the benzene-insoluble portion crystallised from dilute alcohol in colourless plates m.p. 165° (effe).

(Chatterji, Loc. cit. gives 159°).

(Found: C, 52.0; H, 6.0; calc. for $\text{C}_{10}\text{H}_{14}\text{O}_6$ C, 52.2; H, 6.1 per cent). The acid is soluble in alcohol, acetone, and acetic acid, but sparingly soluble in benzene, and petrol. Its calcium and barium salts are soluble while the lead and copper salts are insoluble in hot water.

The anil-anilide was obtained by heating the mixture of the acid (0.8g .) and aniline (1g) at $170-175^\circ$ for three hours. The resulting solid mass was taken up in ether, and washed alternately with dilute HCl and ammonia, dried, recovered and crystallised from dilute alcohol when needles melting at 156° were obtained. (Found: C, 72.7; H, 6.3; $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2$ requires C, 72.9; H, 6.0 per cent) *The p-Tolyl-p-toluidide* prepared in an indential

manner from the acid (0.5g.) and p-toluidine (0.8g.) crystallised from dilute alcohol in small needles m.p. 189-190°.

(Found: C, 73.5; H, 6.8. $C_{24}H_{26}O_8N_2$ requires C, 73.8; H, 6.7 per cent).

Preparation of Ethyl 1-cyano-3-methylcyclopentane-1- α -cyano-succinate.

This was prepared in an analogous manner using 3-methylcyclopentanone-cyanohydrin (12.5), sodium (2.3g.), ethyl cyanoacetate (12.5g.), absolute alcohol (30 c.c.) and ethyl bromacetate (12c.c.). The yield of the condensation product which boiled at 205°/12m.m. was 40 per cent.

(Found: C, 62.5; H, 7.2; $C_{16}H_{22}O_4N_2$ requires C, 62.7; H, 7.2 per cent).

Hydrolysis of the ester to 1-Carboxy-3-methylcyclopentane-1- α -succinic acid.

The ester was hydrolysed as in the previous case, and the acid which was isolated in an identical manner was triturated with benzene and finally crystallised from dilute alcohol in thick, white plates m.p. 144°. Its calcium and barium salts were soluble, while the lead and copper salts were insoluble in hot water. The acid is very soluble in the usual hydroxylic solvents, while sparingly soluble in the non-hydroxylic solvents.

(Found: C, 54.0; H, 6.5. $C_{11}H_{16}O_6$ requires C, 54.1; H, 6.5 per cent). The *Tolyl-toluidide* was prepared by heating the acid (0.5g.) with p-toluidine (0.9g.m.) at 180° for two hours. The product, after the usual purification, crystallised from the mixture of benzene-petrol in small plates melting at 167° (previous sintering). (Found C, 74.1; H, 7.0; $C_{28}H_{28}O_8N_2$ requires C, 74.3; H, 6.9 per cent).

Preparation of α - α -dimethyltricarballic acid.

Ethylsodiocyanoacetate (Na=5.4g.; ethyl cyanoacetate=30g.; absolute alcohol=60cc.) was slowly added to a solution of acetone-cyanohydrin (20g.) in absolute alcohol (20c.c.). After keeping the mixture at room temperature for 48 hours, ethyl bromacetate (40g.) was added in four lots, the mixture again kept at the room temperature for 24 hours, and refluxed on water-bath till the solution was neutral (24 hours). Much of the alcohol was distilled off, and the oil precipitated on the addition of water was extracted with ether, dried and distilled under reduced pressure when three

fractions were collected: (1) b.p. 90-120/6m.m. (2) b.p. 120-165/6m.m. (3) b.p. 178-182/6 m.m. The first fraction was rejected, while the second fraction was again treated with ethyl bromoacetate in presence of sodium ethoxide, and worked up as before, when a further quantity of an ester b.p. 178-182/6m.m. was obtained. The total yield of the ester b.p. 176-178/5m.m. amounted to 45 per cent, and was found to be *Diethyl 2-methyl-3:3-dicyanobutane-3:4-dicarboxylate*.

(Found: C, 58.5; H, 6.8; $C_{13}H_{18}O_4N_2$ requires C, 58.6; H, 6.7 per cent).

Hydrolysis of the ester to α - α -Dimethyl tricarballic acid.

The solution of the ester (20g.) in concentrated H_2SO_4 (40c.c.) after being kept over-night was diluted with water (80c.c.) and heated on sand-bath under reflux for 20 hours. The cold solution was extracted with ether, and the acidic products were extracted from the ethereal solution with sodium carbonate. An oily acid which solidified slowly was precipitated on acidifying the alkaline solution with concentrated hydrochloric acid, and extracted with ether after saturating with ammonium sulphate. The crude acid (m.p. 120-125°) was twice refluxed with benzene, and the melting point rose to 160°. When crystallised from water containing hydrochloric acid, small needles of *α - α -dimethyltricarballic acid* melting at 160° were obtained. (Chatterji, Loc. cit. gives the m.p. 156° while Clemons and Welch, Loc. cit. give 152°). (Found: C, 47.3; H, 6.0; calc. for $C_8H_{12}O_6$ C, 47.0; H, 5.8 per cent). The benzene solution, on concentration deposited an acid m.p. 136° which was identified, by m.p. and mixed up as *α - α -dimethylsuccinic acid*.

The Anil-Anilide prepared as usual crystallised from benzene-hexane mixture in needles melting at 140°. (Found: C, 71.2; H, 6.0; $C_{20}H_{20}O_2N_2$ requires C, 71.4; H, 5.9 per cent).

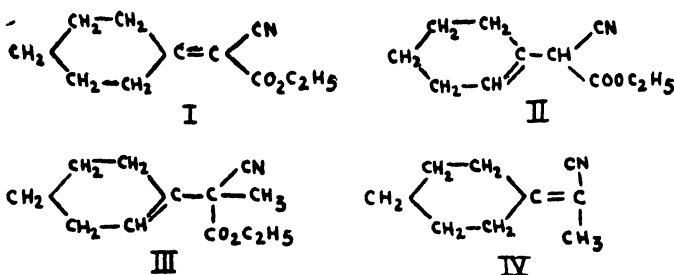
The p-Tolyl-p-toluidide was prepared by heating the mixture of the acid (0.5g.) and p-toluidine (1g.) for two hours at 210-220°, and purified as usual. On crystallisation from dilute alcohol, needles melting at 170° were obtained. (Found: C, 72.6; H, 6.7; $C_{22}H_{24}O_2N_2$ requires C, 72.5; H, 6.6 per cent).

THE METHYLATION OF ETHYL METHYL-CYCLOHEXYLIDENE CYANOACETATES AND REDUCTION OF ETHYL 2-METHYLCYCLOHEXYLIDENE CYANOACETATE

By

R. D. DESAI AND G. S. SAHARIYA.

Kon and his co-workers* have shown that ethyl Cyclohexylidene Cyanoacetate which reacts in the α - β -form (i) with regard to the addition of potassium cyanide tautomerises to the β γ -form, (ii) when methylation in the presence of sodium ethoxide is carried out. They have also shown that the methylated ester (iii) loses carbethoxy group as ethylcarbonate when warmed with sodium ethoxide forming α -cyclohexylidene-propionitrile (iv).



During the course of the synthesis of the various methylcyclohexane-1-carbonyl-1-acetic acids,† we happened to prepare considerable quantities of 4-methyl, 3-methyl, and 2-methyl-cyclohexylidene cyanoacetates. We thought it worth while to study their methylation in the presence of sodium ethoxide to ascertain the influence exerted by the methyl group on the course of this change. It was found that all the esters behaved similarly and

* Kon and Co-workers, J. C. S. (1923), 123, 1369.

† Desai, Hunter, Khan and Sahariya, J. (1936), 416.

closely resembled ethyl Cyclohexylidene Cyanoacetate. Thus the methyl group in the Cyclohexane ring dose not seem to influence perceptibly the α - β - $\beta\gamma$ -change.

Vogel and Oomen,* while studying the reduction of ethyl 4-methyl, and 3-methylcyclohexylidene Cyanoacetates by aluminium amalgam observed the formation of bimolecular products, in addition to the methylcyclohexyl cyanoacetates which are the main products. When ethyl 2-methylcyclohexylidene cyanoacetate was reduced by the same method, the formation of the bimolecular product was almost negligible, and ethyl 2-methylcyclohexyl cyanoacetate was formed as the main product. On alkaline hydrolysis, it gave 2-methylcyclohexyl malonic acid.

EXPERIMENTAL

The various ethyl methylcyclohexylidene cyanoacetates required for the purpose were prepared by the method of Lapworth and McRae† as modified by Desai, Hunter, Khan and Sahariya‡.

Methylation of Ethyl 4-methylcyclohexylidene Cyanoacetate and formation of Ethyl α -Cyano- α -4-methylcyclohexenyl propionate.

A deep red solution was produced when ethyl 4-methylcyclohexylidene cyanoacetate (16g.), was added slowly to sodium ethoxide (2g. Na; 40c.c., abs. alcohol). After adding methyl iodide (20g.), the mixture was allowed to stand at the ordinary temperature for one hour, heated on water-bath for one hour, and diluted with water. The precipitated oil was extracted with ether, dried, recovered and distilled when it boiled at 152-154°/12mm. (Found: C, 70.4; H, 8.6; $C_{13}H_{19}O_2N$ requires C, 70.6; H, 8.6 per cent).

Its chloroform solution added bromine very readily showing that it was a $\beta\gamma$ -unsaturated compound.

α -4-methylcyclohexylidene-1-propionitrile.

The above ester (4g.) was added to a solution of sodium (0.7g.) in methyl alcohol (15c.c.), kept at 35°c. for five hours and water was added. The precipitated oil which was extracted with

* Vogel and Oomen, J. (1930), 768.

† Lapworth and McRae, J. (1922), 121, 2741.

‡ Desai, Hunter, Khan and Sahariya, (1936), 416.

ether and dried over calcium chloride distilled at $106^{\circ}/12\text{m.m.}$ and had the familiar odour of an unsaturated nitrile. It neither added up bromine nor condensed with cyanacetamide in presence of sodium ethoxide. (Found: C, 80.2; H, 10.1; $\text{C}_{10}\text{H}_{15}\text{N}$ requires C, 80.5; H, 10.0 per cent).

It was oxidised by potassium permanganate solution to 4-methylcyclohexanone.

Ethyl α -cyano- α -3-methylcyclohexenyl Propionate prepared from 3-methylcyclohexylidene cyanoacetate, like ethyl α -cyano- α -4-methylcyclohexenyl propionate boiled at $146\text{--}147^{\circ}/12\text{m.m.}$; and decolorised bromine rapidly in chloroform solution. (Found: C, 70.5; H, 8.6; $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}$ requires C, 70.6; H, 8.6 per cent).

α -3-methylcyclohexylidene-1-propionitrile was similarly prepared from the above ester as in the case of α -4-methylcyclohexylidene-1-propionitrile, had the same odour and boiled at $107\text{--}108^{\circ}/12\text{m.m.}$ It did not react with bromine, and cyanacetamide. (Found: C, 80.1; H, 10.2; $\text{C}_{10}\text{H}_{15}\text{N}$ requires C, 80.5; H, 10.0 per cent). Oxidation with KMnO_4 solution gave 3-methylcyclohexanone. *Ethyl α -cyano- α -2-methylcyclohexenyl propionate*, similarly prepared boiled at $144\text{--}145^{\circ}/12\text{m.m.}$ and combined with bromine rapidly in chloroform solution.

(Found: C, 70.4; H, 8.7; $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}$ requires C, 70.6; H, 8.6 per cent). *α -2-methylcyclohexylidene-1-propionitrile* prepared by the usual method from the above ester boiled at $1.0^{\circ}/12\text{m.m.}$ gave the usual smell and did not combine with bromine and cyanacetamide, but was readily oxidised by potassium permanganate solution to 2-methylcyclohexanone (Found C, 80.2; H, 10.2; $\text{C}_{10}\text{H}_{15}\text{N}$ requires C, 80.5; H, 10 per cent).

Reduction of Ethyl 2-methylcyclohexylidene Cyanoacetate to Ethyl 2-methylcyclohexylcyanoacetate.

The unsaturated ester (10g) was added to aluminium amalgam (16g.) covered with moist ether (300c.c.). Having set aside the contents of the flask for 24 hours, the precipitated sludge was filtered off, washed with ether, the combined ether extract dried and distilled to recover the ester which boiled constantly at $135\text{--}136^{\circ}/12\text{m.m.}$ (Found: C, 68.5; H, 9.1; $\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}$ requires C, 68.9; H, 9.0 per cent).

2-methylcyclohexylmalonic acid.

A mixture of the above ester (5g.), absolute alcohol (15c.c.), caustic potash (5g.) and water (15c.c.) was heated on water bath under reflux till the evolution of ammonia was complete (48 hours). After the removal of alcohol, and the extraction of neutral impurities with ether, the alkaline solution, on acidification with concentrated hydrochloric acid gave a solid which crystallised from benzene in small plates melting at 154° .

(Found : C, 59.8 ; H, 8.0 ; $C_{10}H_{14}O_4$ requires C, 60.0 ; H, 8.0 per cent).

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A STUDY OF THE DEHYDRATION PRODUCT OF CHLORAL-3:5-DICHLOROSALICYLAMIDE

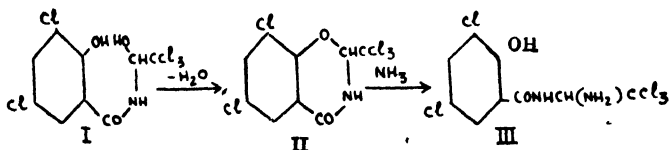
By

(THE LATE) N. W. HIRWE AND K. N. RANA

Chloral-3:5-dichlorosalicylamide (I) (Hirwe and Rana, *Ber.*, 1939, 72, 1351-1353), when treated with conc. sulphuric acid or acetic anhydride in an alkaline medium, loses one molecule of water, and, in view of the following observations, the resulting product has proved to be 6:8-dichlorobenzo-2-trichloromethyl-metoxazone (II) and not the ethylidene type of compound,

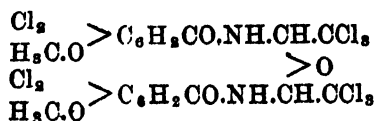


- (i) The compound is insoluble in alkalis.
- (ii) It does not give colouration with ferric chloride, showing the absence of the phenolic hydroxy group.
- (iii) A monoacetyl derivative is obtained.
- (iv) With ammonia a new compound (III) is obtained which is (a) soluble in alkalis, (b) gives red colouration with ferric chloride, (c) forms salts with mineral acids, (d) yields a diacetyl derivative and (e) with nitrous acid the parent compound (I) is regenerated.
- (v) When the product is heated with dilute NaOH, 3:5-dichlorosalicylic acid is obtained.



The fact that dehydration entirely from the side chain does not take place giving rise to the ethylidene type of compound even when the *o*-hydroxyl group is protected, lends a considerable support to the formation of the oxazine ring. Thus when chloral-3:5-dichloro-2-methoxybenzamide is treated with acetic anhydride

in an alkaline medium, the compound obtained is an α -anhydro-derivative :



(Hirwe and Rana, *J. Univ. Bom.*, 1938, 7 (3), 174-177); in this case one molecule of water is eliminated from two molecules of the chloralamide.

Instances of a similar ring formation have been recorded in the literature (Mc Connan and Titherley, *J. C. S.*, 1906, 89, 1318 : Titherley, *ibid.*, 1907, 91, 1419-1425 : Keane and Nicholls, *ibid.*, 1907, 91, 266 : Hicks, *ibid.*, 1910, 97, 1032). In all these cases, on condensation of salicylamide with benzaldehyde or paraldehyde, either benzo-metoxazone alone or a mixture of the compound and ethylidene or benzylidene compound is obtained without the isolation of the intermediate compound of the aldol type,



compound of the aldol type in the present work is thus of interest, and provides additional evidence for the benzo-metoxazone structure assigned to such compounds.

The metoxazone compound has been assigned the structure (II), although the alternative iminohydroxy structure is also theoretically possible.

Hirwe and (Miss) Gavankar* have previously directly obtained a similar metoxazine compound by condensing 5-nitrosalicylamide with chloral. The compound, when heated with ammonia, gave the usual α -amino derivative, transformed by nitrous acid into the α -hydroxy compound.

EXPERIMENTAL

6 : 8-Dichlorobenzo-2-trichloromethylmetoxazone (II)-Method I.—Chloral-3 : 5-dichlorosalicylamide (5 g.) was dissolved in conc. sulphuric acid (20 c.c.). After about 24 hours the solution was poured over ice when a white solid separated. It crystallises from alcohol in shining, minute plates : m.p. 176-7°. It gave no colouration with ferric chloride. (Found : C, 32.76 ; H, 1.45 ; N, 4.42 ;

* Private communication.

Cl, 52.98; $C_9H_4O_3NCl_5$ requires Cl, 32.45; H, 1.19; N, 4.17; Cl, 52.91 per cent).

Method II. To an alkaline solution of chloral-3:5-dichlorosalicylamide (2 g. in 20 c.c. 10 per cent NaOH solu.) acetic anhydride (2 c.c.) was added with constant stirring and keeping the temperature below 15° . The reaction mixture was then kept in a refrigerator overnight. The solid that separated was identified with that obtained by Method I mentioned above.

The *acetyl derivative*, prepared from the compound (1 g.), acetic anhydride (5 c.c.) and conc. H_2SO_4 (2 drops), crystallises from alcohol in white needles: m.p. $123-5^\circ$. It gave no colouration with ferric chloride. (Found: Cl, 47.36; $C_{11}H_6O_3NCl_5$ requires Cl, 47.02 per cent).

α -Amino-chloral-3:5-dichlorosalicylamide (III).—The finely powdered benzometoxazone was suspended in liq. ammonia (D. 0.888) and warmed on a water bath until a greater portion of the solid went into solution. The undissolved solid was filtered off, and the clear solution was heated to drive off the excess of ammonia; it was then neutralised with just the necessary amount of acetic acid. The solid that separated was crystallised from alcohol: colourless plates, m.p. $125-7^\circ$. It gave a red colouration with ferric chloride. (Found: N, 7.43; Cl, 50.23; $C_9H_7O_3N_2Cl_5$ requires N, 7.95; Cl, 50.36 per cent).

The *acetyl derivative*, prepared as before, crystallises from alcohol in white, silky needles: m.p. $207-8^\circ$. It gave no colouration with ferric chloride. (Found: Cl, 40.62; $C_{13}H_{11}O_4N_2Cl_5$ requires Cl, 40.66 per cent).

The *Hydrochloride* crystallises from water in white needles. It gave a red colouration with ferric chloride. (Found: Cl, 54.92; $C_9H_5O_3N_2Cl_6$ requires Cl, 54.76 per cent).

The *Sulphate* also, crystallises in white needles and gives a red colouration with ferric chloride. (Found: S, 4.17; $C_{13}H_{10}O_8N_4Cl_1(Cl_{10})S$ requires S, 3.99 per cent).

Action of Nitrous Acid on (III).—The base (2 g.) was dissolved in dil. hydrochloric acid and an aq. solu. of sodium nitrite (0.4 g.) was slowly added with constant stirring, when a solid began to separate. The mixture was gently warmed on a water bath to complete the reaction. It crystallises from alcohol in

bluish-white, shining prisms : m.p. $158-9^{\circ}$ with decomposition. Its mixed m.p. with an authentic specimen of chloral-3: 5-dichlorosalicylamide showed no depression.

Thanks are due to the University of Bombay for the award of a research grant to one of the authors (N. W. H.).

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Bombay.

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ADULTERATION AND CONSTANTS OF GHEE

By

N. S. DOCTOR AND B. N. BANERJEE

The problem of detection of adulteration of ghee is getting complicated every day as scientific knowledge is being used in the process. Unscrupulous merchants are resorting to tactics that will make the task difficult for chemists and analysts. Hydrogenated oils and fats are coming in handy in this connection, and there are a very wide range of products to choose from, to blend a mixture that will resemble ghee in most of its characters.

Ghee is a physiological product and its chemical and physical criteria are dependent on breed, feed and other factors. The provincial governments of India are not unanimous on the chemical and physical standards of ghee. Cow ghee and buffalo ghee show definite variations in their constants. Lately, the Marketing Board has formulated physical and chemical constants for the grading of ghee.

It is not difficult to prepare artificially a blended ghee having the same refractive index, the same amount of water in soluble fatty acids, the same saponification value, and the same iodine value as the normal butterfat. Vitamins can also be incorporated. The artificial ghee can be made to possess satisfactory digestibility, palatability, and energy giving property. The energy value of different edible oils and fats are practically the same. There is no definite evidence to prove that any particular fatty acid glyceride is indispensable like any of the amino acids of the proteins. In a properly made ghee substitute all those properties can be incorporated and already a very large quantity of such products are on the Indian market. The problem is not the question of merit or demerit of the blended product but the sale

of artificial ghee as pure ghee. The reason for this is not far to seek as genuine ghee sells at about a rupee a pound while the artificial product can be had four times the quantity for the same cost.

The Reichert-Miessl value indicates the extent to which the steam volatile, water soluble fatty acids (low molecular weight acids mostly Butyric and Caproic) are present in fat. Butter-fat or ghee contains much higher amounts of these acids than does any other fat (at present known) from which it might be desirable to distinguish it. Hence the importance of R. M. value in the grading of ghee. No doubt the constants other than R. M. value form also the criterion for purity and quality of ghee, still most of them can be manipulated artificially. Thus, by using a suitable combination of cocoanut oil with the ground nut oil or any other suitable fat or mixture, constants other than volatile acids (R. M., and Polenske values) can be manipulated. Texture, Refractive Index, and Iodine values can be manipulated by the hydrogenation of the fat. All these render R. M. value practically conclusive as a test for ghee, pending any synthetic introduction of butyric acid into vegetable ghee substitutes.

Unfortunately, the R. M. value for ghee is not a constant quantity. It varies between wide limits depending upon various factors such as, breed, feed, health, environmental and climatic conditions, etc., of the animal. Also the R. M. and Polenske values are of an empirical nature and do not purport to indicate the whole of either water-soluble or water insoluble fatty acids volatile in steam, which are present in the original fat. It is obvious that separation by means of steam distillation must at least be related, since, if the distillation be continued until the last traces of an acid (*e.g.*, caprylic) have come over a certain amount of next higher acid or acids will also have accompanied it: and although the volatility in steam rapidly diminishes as the molecular weight increases, it is definitely appreciable upto lauric and myristic acids. Nevertheless, by working under controlled conditions as to dimensions of apparatus and time of distillation (Report of Analytical Methods Committee, 1936), comparable results can be obtained which are an index of the volatile fatty acids, present in the original fats.

Many workers, however, have noticed that samples of genuine ghee are often met with which do not give figures within the

limits and in fact, would, in view of Polenske's limit, point to adulteration. Conversely ghee samples often give values which would allow to considerable adulteration with cocoanut oil and other mixtures before R. M. and Polenske's limits were exceeded. Therefore, it is necessary to exercise due deliberation before reporting any sample of ghee as adulterated on the basis of the R. M. value alone. Even for samples of ghee giving the R. M. value within the specified limits or higher, the possibility of adulteration is by no means remote and before such samples are reported as genuine, other corroborative tests should be performed.

The problem is more complicated in our country, where large quantities of ghee are being prepared by small stock owner, owning only one or two cows or buffaloes, generally half-starved and kept under unhygienic conditions. Further, the concentrates for feeding milch cattle in different areas depend on the oil-seed or the grain grown in that area. Thus, in Gujarat (Kathiawar) and black cotton soil areas, only cotton seed is fed; in certain areas only cocoanut cake and in others gingili or groundnut cake. This has brought a certain amount of confusion in fixing standards for testing the purity and the grading of ghee. For instance, ghee coming from Kathiawar is known to give abnormally low R. M. value and this is attributed to the exclusive feeding of cotton seed. Under these circumstances, accurate data on the range of variation of the analytical constants of ghee due to various factors that affect them, would prove useful in testing purity and quality of ghee.

With a view to studying the effect of feed, breed, method of preparation of ghee on the composition of butterfat, an investigation was conducted at the Imperial Dairy Institute Farm, Bangalore, in close consultation with the Imperial Dairy Expert (a detailed account of which will be published later). Some of the results obtained by us have been recorded in tables at the end to show the characteristic effect of feed, breed, etc., on the constants of ghee. Method of preparation does not affect the constants of ghee, however, the texture, moisture, acidity and solids not fat, are dependent on the care taken in the preparation of ghee. Different breeds of cattle show marked difference in the composition of butter-fat. It is evident from the results that the composition of butter-fat of animals fed with oil cakes appear to become similar to that of the oil. Also, the constants appear to vary in a charac-

teristic way. Thus, in the case of animals fed with oil cakes there is a fall in the R.M. and saponification values while there is a rise in the Iodine values.

The physiological characters of ghee also should be taken into consideration along with the physical and chemical constants. The carotene and vitamin-A content slightly decreases with the feeding of oil cakes and increases with the feed rich in carbohydrate and green pasture. Feeds rich in carotenes give rise to higher carotene content in the milk fat. The vitamin-A content of ghee expressed in Lovibond Bule Units has been found to vary from 15 to 20 units per gram in fresh sample of ghee. Deeper yellow colour due to carotene is always associated with higher vitamin-A content. Cow ghee is deeper than buffalo ghee in yellow colour. This depends to a certain extent on the carotenoid feed of the animal. The yellow colour is, however, unmistakable in the ether-soluble unsaponifiable matter. The yellow colour due to lactochrome bodies always separates out in the aqueous layer. All vegetable oils and fats except palm kernal oil are devoid of carotene bodies.

The richness of vitamin-A content of any sample of ghee has been observed to be proportional to its flavour. In India as a matter of practice, odour has been the rough and handy criterion of judging the quality of ghee. Cow and Buffalo ghee have characteristic flavour and possess well defined constants. The colour and odour of ghee are very useful criteria for distinguishing butter-fat from foreign fat.

It is therefore necessary to take into consideration the cumulative effect of all constants, physical, chemical and physiological along with the history of the origin of the sample while judging the quality and purity of ghee. With this in mind, a careful critical examination of the various constants of ghee would greatly facilitate the already difficult task of grading and determining the quality and adulteration, if any, of ghee.

METHOD OF PREPARATION AND BUTTER FAT.

Sample	Description	R. M. value	Polenske value	Saponification value
1	Fresh cream butter melted into ghee.	33.0	1.9	238.0
2	Cream soured for 12 hours.	31.3	1.9	239.1
3	„ 24 hours.	31.2	1.8	239.4
4	„ 48 hours.	31.2	1.8	237.8
5	Butter (2) kept for 11 days at room temperature (fungus and mould growth).	31.0	1.8	238.1
6	Butter (2) kept for 15 days.	31.1	1.7	238.8
7	Butter (8) (ghee prepared by boiling off moisture from butter.)	31.0	1.8	239.0
8	Curd butter, fresh, melted into ghee	31.7	1.8	238.2
9	Butter (8) kept for 2 days.	31.1	2.0	239.2
10	„ kept for 4 days.	30.6	1.9	239.8
11	„ kept for 7 days.	31.1	1.7	238.0
12	„ (11) (ghee prepared by boiling off moisture)	31.1	1.7	239.4
13	Butter (8) kept for 15 days.	30.8	1.7	238.8
14	(No. 13) ghee prepared by boiling off moisture.	30.6	1.7	239.0

BREED CHARACTERISTICS OF BUTTER FAT

	Butter			Butter Fat								Carotene mgm. per 100 gm.	Vitamin A, R. V. per gram	
	Moisture p. c.	Fat p. c.	Curd p. c.	M. P. 00C.	R. Index at 400C.	B. R. reading at 400C.	R. M. value	Polenske value	Kirchner value	Saponification value	Iodine No. (Wij's)			p. c. of free fatty acids calculated as oleic acid
Sindhi	Sample 1	15.6	84.0	0.4	37.00	1.4556	25.6	2.3	20.0	225.1	39.0	0.91	0.52	16.4
	2	14.9	84.8	0.3	37.20	1.4556	26.0	2.2	20.2	223.2	39.1	0.90	0.50	15.0
	3	15.1	84.6	0.3	37.20	1.4556	26.4	2.2	20.3	224.8	39.0	0.83	0.48	15.8
	4	16.7	84.8	0.5	37.40	1.4556	25.8	2.3	20.0	223.0	39.0	0.85	0.52	16.0
	5	14.0	85.6	0.4	37.20	1.4556	25.6	2.3	20.0	222.8	38.8	0.83	0.46	15.6
	6	13.2	86.4	0.4	37.00	1.4556	26.0	2.3	20.0	224.0	38.8	0.92	0.48	15.2
Gir	Sample 1	15.8	83.9	0.3	36.00	1.4553	26.8	2.2	21.6	226.8	39.3	0.35	0.48	16.0
	2	14.9	84.7	0.4	36.20	1.4553	27.0	2.2	22.0	227.5	39.9	0.40	0.40	15.4
	3	14.2	85.3	0.5	36.40	1.4553	27.4	2.3	22.0	227.0	39.0	0.42	0.38	15.0
	4	18.3	81.2	0.5	36.20	1.4553	27.8	2.3	22.0	226.9	39.2	0.34	0.38	14.8
	5	16.4	83.4	0.2	36.20	1.4553	27.8	2.3	22.0	226.9	39.2	0.34	0.38	14.8
	6	15.1	84.6	0.3	36.20	1.4553	28.2	2.3	22.4	226.4	39.0	0.43	0.33	14.6
Murram-Buttalo	Sample 1	14.3	85.4	0.3	36.80	1.4549	30.4	1.5	26.7	231.4	31.5	0.80	0.05	14.0
	2	13.9	85.9	0.2	37.00	1.4549	30.6	1.5	26.7	232.2	30.8	0.70	0.05	14.8
	3	14.7	85.0	0.3	37.00	1.4549	30.9	1.5	26.7	231.8	31.0	0.66	0.05	14.2
	4	13.5	86.2	0.3	36.80	1.4549	31.0	1.5	26.8	232.0	31.4	0.62	0.05	14.0
	5	13.2	86.8	0.2	37.00	1.4549	30.2	1.5	26.6	231.2	31.2	0.67	0.05	14.6
	6	12.6	87.1	0.3	37.00	1.4549	30.4	1.5	26.6	231.0	31.4	0.50	0.05	14.2

FEED COMPOSITION AND GHEE

Concentrate SL No. DIET Roughage	FEED COMPOSITION AND GHEE					
	I	II	III	IV	V	VI
	GROUNDNUT CAKE 50 p.c. groundnut cake + 50 p.c. wheat bran 50 lbs. Rhodes and guinea grass	GINGILI CAKE 50 p.c. wheat bran plus 50 p.c. gingili cake Same as in I	LINSEED CAKE 50% wheat bran + 50% linseed cake Same as in II	COTTON SEED MEAL 50% wheat bran + 50% cotton seed Same as in I	COCONUT CAKE 50% wheat bran + 50% coconut cake Same as in I	CEREAL & GRASS 40% wheat bran + 20% wheat, oats, barley, crushed each 10 lbs. lucerne and rest guinea and Rhode.
No. of cow	261	279	280	285	289	294
Quality of ghee (1st & 2nd period same)	Order of merit	Third	Fifth	First	Fourth	Best
	Body	Soft and leaky	Very soft & leaky	Quite firm	Quite attractive and hard	Firm
	Texture	Satisfactory, medium hard	Oily	Satisfactory grains	Satisfactory grain smaller than IV	Satisfactory, gra- nular texture
	Colour	Good Fair yellow	Light yellow	Fair yellow	Fair yellow	Deep reddish yellow
	Flavour	Satisfactory, ghee flavour	Indications linseed oil	Satisfactory ghee flavour	Indicating cooco- nut oil	Quite satisfactory

No. of cows			251 275	279 291	280 290	265 270	289 294	
R. M. value	...	0	30	26	29.1	25.9	26.9	28.0
		I	25.2	26.9	24.9	25.1	26.5	29.1
		II	25.8	26.1	24.6	23.6	26.5	29.1
R. Index	...	0	42.3	42.3	42.6	43.7	43.7	42.5
		I	43.7	43.7	44.0	43.7	41.1	41.0
		II	45.0	44.6	45.2	43.7	41.0	40.0
Polenske value	...	0	2.5	2.5	2.4	2.3	2.5	2.5
		I	2.0	2.4	2.4	2.0	2.9	2.9
		II	2.1	2.2	2.1	2.1	3.0	3.0
Kirschner value		0	23.3	21.1	22.9	21.0	22.0	23.3
		I	17.0	20.5	18.4	20.0	22.0	23.2
		II	17.2	20.6	18.2	18.1	22.0	23.3
Saponification value		0	229.2	229.2	227.0	224.0	225.0	229.2
		I	223.0	224.8	220.8	221.6	230.6	229.8
		II	223.8	224.2	217.6	219.8	229.6	230.0
Iodine value	...	0	36.0	36.1	37.7	34.0	36.3	36.0
		I	42.2	42.3	39.0	37.2	28.3	29.5
		II	37.0	40.1	42.1	37.3	26.8	29.8
Vitamin A	...	0	16.4	15.3	16.2	15.0	15.0	16.4
(Lovibond blue units								
per gm.)	...	I	11.1	12.3	9.0	12.4	11.0	18.4
		II	11.0	11.4	8.3	12.0	10.9	18.8
Carotene (in mgm.								
per 100 gm.)	...	0	0.52	0.38	0.52	0.41	0.41	0.52
		I	0.86	0.41	0.31	0.31	0.38	0.60
		II	0.41	0.41	0.27	0.40	0.36	0.61
p.c. free fatty acids		0	0.14	0.42	0.50	0.44	0.24	0.14
present as oleic acid		I	0.28	0.24	0.30	0.28	0.50	0.21
		II	0.30	0.32	0.41	0.35	0.42	0.30

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HEAVY ELECTRON*

By

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1. DISCOVERY OF A NEW PARTICLE

The existence of a particle about two hundred times heavier than an electron was assumed by Yukawa four years ago in trying to explain the proton-neutron interaction within the nucleus of an atom. But it was discovered experimentally only two years back in the course of experimental researches on cosmic rays.

Cosmic radiation is an ionising radiation travelling downwards from the top of the atmosphere. The variation of the ionisation, I , with depth d , from the top of the atmosphere has been studied experimentally and can also be theoretically calculated assuming either that the cosmic radiation consists of charged particles or that it consists of photons. The ionisation depth curve to be expected at high altitudes is different for the two cases. Since the experimentally observed curve is similar to the one to be expected for charged particles, it is considered that cosmic radiation incident at the top of the atmosphere probably consists of charged particles. Charged particles will be affected by the earth's magnetic field and the maximum energy of particles incident at different latitudes will be different. When cosmic radiation falls on matter, two or more ionising particles carrying charges of different signs and with varying velocities are emitted from within a small region. This phenomenon is called a cosmic ray shower. Shower production depends on the energy of the incident radiation.

These several aspects of cosmic ray research have been most carefully investigated and some remarkable facts have been discovered. As a result of the study of the ionisation produced at different depths from the top of the atmosphere, several

* It is now usual to use the name "meson" for this particle. The positive electron is called the positron and the negative electron is called the negaton, the name electron being used for both. Since this terminology is not final, the older names are used in this article,

investigators¹ reported that the absorption coefficient for cosmic radiation at great depths was much lower than that observed at higher levels. This observation can be very simply interpreted by supposing that cosmic rays consist of two components, a soft one and a hard one.

The theory^{2, 3} of cosmic ray showers and of loss of energy of cosmic rays has been worked out. The ideas underlying the theory are as follows: A very high energy electron can produce a number of ionising particles in the following manner. When it passes within the sphere of action of a nucleus, it emits a high frequency radiation (collision radiation) and its energy is correspondingly lessened. This photon if it passes within the field of a nucleus can be converted into a positron-electron pair. A positron cannot live long. When it interacts with an electron, the two particles are destroyed and photons are produced. (Only one photon is produced if the interaction takes place within the sphere of action of the nucleus.). The electron and the photon can again produce photons and positron-electron pairs respectively. The production of a shower out of a single cosmic ray electron can be understood on the basis of these ideas. Besides, the theory gives the correct intensity variation for cosmic rays from the upper layers of the atmosphere downward. The observed absorption of cosmic rays at great depths is markedly different from that given by this theory. It is, therefore, probable that the penetrating component consists of particles different from the soft component. Auger⁴ had very clearly stated this four years ago. He held the view that the soft and hard components consist of different types of particles rather than of particles of different energies.

The investigation of the nature of the penetrating component was, therefore, a matter of considerable importance. By using a suitable lead or other absorber, the soft component could be cut out and the penetrating component obtained fairly free from the soft component. The penetrating component can then be studied in a Wilson cloud chamber under the action of a magnetic field. It is known that for a fast moving particle, ionisation is proportional to the square of its charge. Hence a study of the ionisation of particles in the beginning of their tracks is of no use. All elementary particles generally carry one electronic charge and their ionisations would be indistinguishable. But ionisation due to slow moving particles of the same charge and velocity would be proportional to ~~their~~ masses. It is, therefore, obvious that for obtaining information on the nature of the particles in the pene-

trating component, the tracks of such particles must be obtained towards the end of their range.

A typical experiment carried out on the basis of the above arguments will now be described. Street and Stevenson⁶ arranged their apparatus as follows:—

- Counter No. 1.
- Counter No. 2.
- Lead Block—
- Counter No. 3.
- Wilson Cloud Chamber—
- Three Counters No. 4.

The lead block absorbed the bulk of the soft component. Hence, if counters Nos. 1, 2, and 3 were discharged simultaneously, it would imply that only the hard component was passing through the cloud chamber. If, at this moment, counters No. 4 did not discharge, the particles in the hard component were near the end of ranges while passing through the cloud chamber. The chamber was, therefore, expanded and photographs taken only when the counters Nos. 1, 2, and 3 were discharged, but not counter No. 4. The photographs were taken under the action of a magnetic field. Along one of the tracks obtained, ionisation was greater than that for an electron and less than that for a proton of velocity corresponding to the curvature of the track. This meant that the track was due to a new particle. This particle is called the heavy electron. From measurements of specific ionisation along its track, Street and Stevenson estimated its mass to be about 130 times the electronic mass. Several workers⁶ have since then investigated the matter. Both positively and negatively charged heavy electrons have been found. The mass has been estimated at a few hundred times the electronic mass. The general indication is that the mass is about 200 m_e .

(The existence of the heavy electron was actually forecast by Neddermeyer and Anderson⁷ on the basis of some of their experimental results. But the first conclusive evidence was from the experiments of Street and Stevenson).

2. NUCLEAR THEORY AND THE HEAVY ELECTRON

The first attempt at a theory of nuclear structure assumed that the nucleus consisted of protons and electrons. Since electrons in nuclei did not contribute to nuclear spin, this theory was discarded. After the discovery of the neutron in 1932, attempts were made to

build up a theory of nuclear structure by supposing that nuclei are made up of protons and neutrons. To build up a theory on this basis, we require to know the nature of the forces acting between protons and protons, protons and neutrons and neutrons and neutrons. The stronger the force, the greater the binding energy and hence the greater the stability of the nucleus. The only stable nucleus of mass 2 has a charge of one unit *viz.*, the deuteron. Hence it was tentatively concluded that the most important contribution to nuclear stability arises from forces between protons and neutrons. This conclusion is also borne out by an examination of the mass and charge numbers of heavier nuclei. The law of force between protons and neutrons is unknown. It was empirically suggested⁸ and is based on an analogy between the deuteron and the positive ion of molecular hydrogen, the quantum mechanics of which is well established. The deuteron consists of a proton and a neutron, while the positive ion of molecular hydrogen consists of a proton and a neutral hydrogen atom. The positive ion of molecular hydrogen consists of two protons at an arbitrary fixed distance apart and an electron. There will be a characteristic frequency for the exchange of the electron from one proton to the other. This frequency can be calculated as a function of the distance between the protons, say as $f(r)$. The exchange energy will be $hf(r)$ and the exchange force will be $h f'(r)$. We may look upon this force as responsible for the stability of the hydrogen ion. A similar exchange force was postulated for a proton-neutron interaction and is known as Heisenberg-Majorana exchange force. This exchange force proved remarkably useful in building up nuclear theory. The Heisenberg-Majorana exchange force did not require the exchange of charge as the necessary physical basis for it. If the latter assumption had been made, the theory would have got into difficulties.⁹

To explain β disintegration, however, it became necessary to assume that every real transition from a proton to a neutron and *vice versa* was accompanied by the ejection of a positive or negative electron. Fermi¹⁰ introduced this assumption. He regards the neutron and the proton as different quantum states of a single heavy particle. The transformation from one state to the other is accompanied by the emission of a positive or negative electron. The limiting energy of disintegration is regarded as the unique energy of disintegration. The difference of energy between the latter and a β -particle is supposed to be carried away by a particle of rest-mass zero and no charge, but with a spin of $\frac{1}{2}$. The latter particle is called a neutrino. On the basis

of these ideas, Fermi calculates the relation between the transformation constant, λ , and the disintegration energy E_0 . The force function constants for the proton-neutron inter-action that Fermi assumes in his calculations are different from those obtained as in the arguments outlined above. If the latter are used, disintegration probabilities become greater than actually found.¹¹ There was thus a clear discrepancy between the Heisenberg-Majorana exchange force and Fermi's theory. Attempts were made to remove it.¹²

About this time, Yukawa¹³ successfully attempted a more consistent theory of nuclear structure. It did not however, attract attention till the actual discovery of the heavy electron. Yukawa develops a relativistic theory of the interaction of heavy particles. The fundamental ideas underlying his theory appear to follow very naturally from the earlier work described above. Just as Coloumb forces between electrons and nuclei are related to the emission and absorption of photons similarly short range nuclear forces between protons and neutrons are related to the emission and absorption of a particle. The emission and absorption of this particle only takes place when it is consistent with the principle of conservation of energy. In other cases, the emission or absorption is merely virtual as in the quantum theory of radiation. The mass, m , of the particle in Yukawa's theory is related to the range of nuclear forces, r , by

$$r = \frac{\hbar}{mc}$$

Taking $r = 10^{-12}$ cm, m works out to be of the order of $200m_e$. We see, therefore, that the Yukawa particle is very similar to the electron.

It is, therefore, of considerable interest to know how exactly the above relationship can be obtained. Wick¹⁴ has suggested a very simple derivation of the above equation. Suppose one heavy particle is transformed into another with the emission of a heavy electron. Then the energy involved in the process is at least mc^2 . The time, t , taken by the heavy electron in travelling from one particle to the other is at least r/c . Hence, the energy uncertainty is of the order of $\hbar \frac{c}{r}$. Therefore,

$$mc^2 \sim \frac{\hbar c}{r}$$

i.e. $r \sim \frac{\hbar}{mc}$.

So much for the nature of the particle. To explain β -disintegration,

it is assumed that this heavy electron can interact with electrons and neutrinos. When it exists in a free state, it becomes β -active and disintegrates into an electron and a neutrino. The probability of its disintegration is such that its mean life, T_0 , is given by

$$T_0 = \frac{3h^2}{g^2 mc}$$

where g is Fermi's constant of β -decay and can be taken roughly as 4×10^{-17} . T_0 is about $\frac{1}{2} \times 10^{-6}$ sec. When the heavy electron is moving rapidly, it will live longer owing to relativity change of time¹⁵. The mean time of life is then given by

$$T = \gamma T_0$$

where γ is the ratio of the total energy of the particle to its rest energy.

The theory of Yukawa has recently been generalised and developed by several workers^{15,16}. Yukawa had assumed that the heavy electron obeys Bose statistics and this assumption is almost generally made. This is necessary if the proton-neutron interaction is to take place with the emission or absorption of a single heavy electron. But it has been pointed out recently¹⁷ that the proton-neutron interaction can be explained equally satisfactorily by assuming that heavy electrons obey Fermi statistics if the inter-action occurs with an exchange of a charged and a neutral heavy electron. We shall, however, stick to the old assumption that the heavy electron obeys Bose statistics.

The substance of the present position of the theory can be put as follows: Positive, negative and neutral heavy electrons can exist. Protons and neutrons are considered to be two states of the same heavy particle. Transition from one state to the other occurs with the emission or absorption of a heavy electron. It then follows automatically that positive and negative heavy electrons can exist. The proton-neutron interaction is then satisfactorily explained and an interaction force appears similar to the Heisenberg-Majorana exchange force. The question of β -disintegration has already been referred to. There is satisfactory agreement between theory and experiment over a wide range. Nuclear theory requires a close-range proton-proton interaction which is not negligible. This is explained by supposing that the interaction between two protons occurs with the emission or absorption of a neutral heavy electron. Besides, *the following possibilities have been pointed out*. A positive heavy electron on colliding with a neutron in the presence of other particles may transform the neutron into a fast proton by combining with the

neutron. Under certain circumstances, the absorption of a positive heavy electron by a neutron may lead to the emission of a neutral heavy electron and *vice versa*. A heavy electron may disintegrate into a proton and a neutron.

3. EVIDENCE FOR THE EXISTENCE OF THE NEUTRAL HEAVY ELECTRON.

In the above theoretical discussion, the existence of a neutral heavy electron has been assumed. Its existence cannot be proved directly but can be inferred indirectly. Although the evidence is not conclusive, it is fairly satisfactory and is as follows¹⁸: At great depths,¹⁹ it was found that ionisation due to cosmic rays was due to shower particles and not to single ionising rays. This implies that there is a non-ionising shower-producing radiation. A block of iron ¹⁸⁰ of varying thickness was placed between two counters and above both of them. The difference in the number of coincidences was measured. This difference is clearly due to ionising secondaries produced by non-ionising primaries. The latter was found to have the same absorption coefficient as the penetrating component of cosmic rays, which is known to consist of heavy electrons. It is clear that the non-ionising primaries must be neutral heavy electrons.

4. EVIDENCE FOR THE RADIO-ACTIVE DECAY OF HEAVY ELECTRONS.

It has been assumed that the heavy electron is radioactively unstable when in a free state and that it disintegrates into an electron and a neutrino. Experimental evidence in favour of this view has been obtained by a number of workers¹⁹, from cosmic ray measurements. The intensity of the penetrating component under a large thickness of air is found to be much less than that under the same thickness of water or clay. In air, the distance travelled is longer. Hence a greater number of heavy electrons will have disintegrated and the intensity will consequently be less. We will carry out a numerical calculation. The intensity of the penetrating component is found to be half that under water for an equivalent thickness of air corresponding to 60 metres of water i.e. 6×10^8 cms. of air. Therefore, the mean life is $\frac{6 \times 10^8}{3 \times 10^{10}}$ i.e. 2×10^{-4} sec. If the mean energy of rays is taken to be 10^{10} eV and m as $200 m_e$, t_0 works out to be 2×10^{-3} sec. This is a calculation due to Blackett. In all cases, the order of magnitude

comes out to be equal to the theoretical value. But there is a discrepancy between experimental and theoretical values. The mean life depends on the mass of the particle and it has been pointed out recently that the discrepancy between theory and experiment becomes smaller as the mass decreases²⁰.

5. ORIGIN OF THE HEAVY ELECTRONS.

Nothing is definitely known about the origin of heavy electrons. Some experiments indicate that they are probably of secondary origin. Auger describes experiments in which coincident discharges of a number of counters are observed. The results indicate showers spread over an area of 25 square meters and containing over a thousand particles. The particles have a range of 15 cm. in air which shows that the particles are heavy electrons. Hence a whole shower of heavy electrons appear to be created in one act²¹. It is, therefore, assumed that heavy electrons are produced in the upper layers of the atmosphere by the primary electrons and photons. A theory on this basis has been worked out²².

6. NOMENCLATURE

So far the new elementary particle is referred to as the heavy electron. But the literature on the subject has not adhered to any one name. It has been called dynaton, barytron, yukon, x -particle, u -particle, mesotron and meson. The name mesotron was suggested by Anderson and Neddermeyer²³, because the heavy electron is a particle of mass intermediate between those of electrons and protons. Bohr has suggested that it is more appropriate to call it "meson". The neutral heavy particle is called a neutretto¹⁸.

7. CONCLUSION.

In the present state of the subject, the foregoing discussions must be considered tentative. Particles carrying unit positive or negative charge and having a mass about a few hundred times the mass of the electron have been discovered. The existence of similar particles carrying no charge has been indirectly inferred. There is at present no accurate estimate of the mass of these particles.

These particles, when in a free state, are considered radioactively unstable, disintegrating into electrons and neutrinos. The available experimental evidence is in favour of this view.

Since the existence of the neutrino itself is not definitely established, it is safer to assert that the new particles are radioactively unstable and that electrons are produced as a result of the disintegration. These particles are considered to be of secondary origin. They are supposed to be produced in the upper layers of the atmosphere by the incident primary electrons and photons.

These particles play a very important part in recent developments of nuclear theory but it must be emphasised that as yet they have not been observed in the laboratory experiments on nuclear disintegration. The mathematical theory of these particles assumes that they have no spin and, although it is engaging the attention of several investigators, it has not yet reached a very satisfactory stage²⁴.

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THE PROBLEMS OF NOISE

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INTRODUCTION

With the growth of civilization, the mechanical age has firmly set in and has brought in its turn the undesired by-product of machines which are now increasingly employed not only for industrial but even domestic purposes and operations. Noise is one of the features of the uncontrolled development of this mechanical age. The modern mechanical transport continues to give intermittent street noise even in residential localities and frequently disturbs the quiet hours of midnight. There are the slammed car-doors, the sudden and violent accelerating of cars, the passing of heavy lorries by the neighbouring road-side and the night traffic by train which contribute in producing a jarring sound. The continuous din of one or other of the modern symbols of mechanical age has almost become a bane to the preservation of national health and efficiency. The effects of

noise are varied and many. For instance, Wagner¹ states that loud continuous noise in a metal factory produces deafness among its workers; noise affects the working of the brain-mass and heart; increases the blood-pressure, causes irregular contraction of the stomach and lowers the manual and mental activity. Similar investigations on the influence of noise and tremors on health have been reported by Katel.²

The last decade has attracted increasing attention towards the problems of noise in various countries. In England, the Departmental Committee of the Ministry of Transport, in conjunction with the National Physical Laboratory have carried out investigations on noise in the operation of mechanically propelled vehicles. Pioneer work in this connection has been done by G. W. C. Kaye³. In U. S. A., Russia, and Germany, scientific investigations on the noise problems are undertaken on behalf of the respective governments. These have led to campaign against unwanted noise. Importance of such investigations becomes greater for the thickly populated and industrial cities, where the incessant traffic and beehive activity in large factories have assumed the proportions of regular nuisance. The measurement of such noise and devising means for its abatement have become a regular feature in several important centres in the western countries. The subject of measurement of noise is highly technical and still more so is the problem of its abatement, in so far as it relates to the study of acoustic properties of various materials. Evolving sound absorbers for injurious noise-levels is a part of this study. In view of the growing importance of this branch in the science of acoustical engineering, it is intended to take a survey of the work accomplished so far, especially in the field of the measurement and abatement of noise.

For the sake of convenience, we shall divide the subject into two parts. In the first, we shall deal with the technical aspect of the measurement of noise and in the second, with the methods of its abatement.

I.

MEASUREMENT OF NOISE

(a) Noise : Its definition and meaning.

There are a number of alternative ways of defining noise. None appears to be satisfactory from all points. Though the

rough working definition is that sound is a noise, when it is treated as a nuisance, it does not bring to us an exact scientific meaning or explanation. Noise may well be defined as an unwanted sound but according to Davis⁴, there are characteristics which define the degree of annoyance, distraction or interference caused by such unwanted sound. He points out that such characteristics may depend upon the hearer, upon his history, his liver or the work he has on hand. They may also depend upon the circumstances attendant upon the production of noise, that is, whether it is unexpected, intentionally offensive or wholly out of place. Without in any way entering into critical discussion of the characteristics at this stage, we can say that the most dominating factor of noise that causes annoyance is its loudness. This is borne out by general experience. However, in view of the general importance which the problem of noise abatement has gained in society for the national well-being, it is appropriate to mention also the legal definition according to which *noise* is said to be "excessive, offensive, persistent or startling sound".

(b) Sound and Noise.

The foregoing definitions and explanations of noise have made it abundantly clear that for any noise to occur, there must be sound produced. It is only when particular adjectives are attached to sound that we call it noise. In other words, the limits set upon the quality and degree of sound enable us to identify it with noise according to legal definition of the latter. To understand noise for scientific purposes one must know the physical meaning of sound and its propagation.

According to established conceptions, sensation of sound is produced by the action on the ear, of longitudinal pressure waves usually in air. For communication of such pressure to surrounding air, there must be vibration or disturbance akin to vibration. According as the pressures in the waves rise or fall, the differences in the quality of sound are registered. If at a given point, the sound pressure varies sinusoidally with time, the sound is said to be a 'pure tone'. A smooth wave-form is associated with 'pure tone' such as that of a tuning fork vibrating with its fundamental pitch. This can be identified with wave-form of fig. 1 (a). If the same tuning fork is struck violently, it will emit a high-pitched note in addition to its fundamental note. The wave-form is slightly different under this condition [fig. 1 (b)]. The wave-form such as that of fig. 1 (c) can be reproduced by sounding together

a number of pure tones of different pitches in the same musical scale. It is said to be a complex tone. Of somewhat the same pattern is obtained the wave-form of a street noise illustrated in

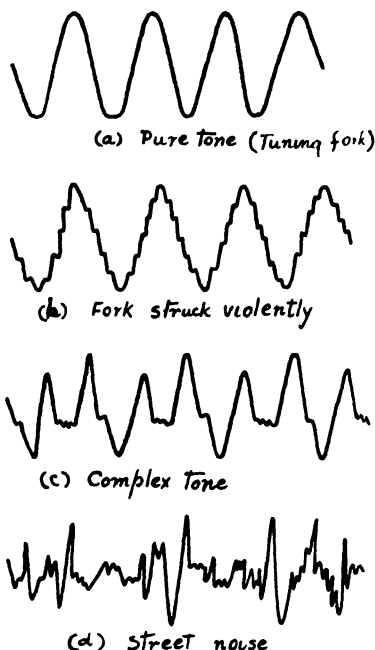


Fig. 1.

fig. 1 (d). We do not call it a pure or complex tone but noise from the fact that it is not of a repeating type, besides being irregular and without any pitch. All the above figures serve to illustrate the essential difference between sound and noise.

Complex noises can thus be regarded as a number of pure tones superimposed. In order to understand the action of a complex noise, one must follow the effect produced by a pure tone. The 'magnitude' of a tone of given frequency may be defined by stating the *instantaneous pressure* at a given point which is proportional to the particle velocity. In the presence of a sound wave, the point in question will have a certain maximum pressure. The difference between it and the static pressure at the point is termed the *instantaneous pressure*. For practical purposes, either mean, peak or root mean square values may be used, but usually *effective sound pressure* is adopted and is known as the *root mean square* (R.M.S.) value of the instantaneous sound pressure.

When it is a question of measuring these pressures for the purposes of noise, we are guided by the effect they produce on our ear. It is ultimately the sensation by which we must judge the pressure fluctuations resulting from a sound wave. This latter is a physical stimulus to the ear and is distinguished from sound sensation to which it gives rise. The greater or smaller magnitude of noise is thus a function of intense or feeble sound sensation. Having considered the sound-wave stimulation, it is necessary to follow the manner in which the ear responds to it.

(c) The Units : decibel

There is a lower limit of pressure which gives rise to sound sensation or sensation of hearing and an upper limit beyond which there is an onset of feeling or pain in the ear. Before sketching these characteristics of the ear, it seems reasonable to understand the units in which the upper and lower limits of the ear are generally indicated or expressed. It is usual to state the limits either as effective pressure or the intensity, the former in dynes per sq. cm., the latter in watts or milliwatts per sq. cm. The audible sound intensities range from about 10^{-16} watts per sq. cm. to about 10^{-8} watts per sq. cm. This range being very large, it is convenient to express the intensity and pressure measurements logarithmically, that is, in decibels. Thus if I_1 , and I_2 are two intensities, they differ by n decibels, where,

$$n = 10 \log -$$

Now since intensity is proportional to the square of the pressure, it follows that

$$\frac{I_1}{I_2} = \frac{P_1^2}{P_2^2}$$

Hence

$$n = 20 \log \frac{P_1}{P_2}$$

$$\text{or } n = 20 \log \frac{V_1}{V_2} \text{ where } V_1 \text{ and } V_2 \text{ are the particle velocities.}$$

It appears from this that decibel is not a unit but the logarithm of a ratio. It is necessary therefore to state from what

lower level or datum line the decibels are reckoned. As a rough indication, decibel is the smallest change in intensity that can be detected by the ear. Churcher, King and Davis⁵ have shown that the least perceptible change in intensity of a pure tone is a function of the intensity and of the frequency and may be less than 0.1 decibel under experimental conditions. It is to be understood however, that decibel does not in any way give a measure of the resulting sound sensation but a measure of the intensity.

(d) Characteristics of the ear.

(i) The threshold intensity :

It has been pointed out already that the dominant measurable feature of noise is its loudness. This is expressed in terms of pressure, intensity or particle velocity in a sound wave. Measurements on the acoustical pressure fluctuations giving rise to sensation of hearing have given interesting results. For a pure tone, the minimum intensity below which it is not audible is termed the *threshold intensity*. This varies with the frequency of the tone. Its value may vary from person to person or is affected by the momentary state of fatigue of the ear or will give higher or lower magnitude according to the presence or absence of other sounds in the background. For an ear of given sensitivity, the threshold intensity might be taken mean effect of four computations as follows :

(1) The smallest *audible* intensity with tone *decreasing* in intensity,

(2) The largest *inaudible* intensity with tone *decreasing* in intensity,

(3) The smallest *audible* intensity with tone *increasing* in intensity, and

(4) The largest *inaudible* intensity with tone *increasing* in intensity.

These four values of threshold may not be coincident but difference between them will be small compared to the probable error of each single determination. The *threshold intensity* will therefore lie in the region where a small increase in intensity will make the tone audible or a small decrease will make it inaudible.

It is to be noted that for the threshold, much greater pressures are needed with low notes than with notes of medium pitch. It is also known that low notes become painful sooner than the medium ones. Variations in sensitivity also arise due to the head orientation of the observer and whether he listens with one ear or with two. These variations are appreciable at medium and higher frequencies. From a large number of observers of normal hearing, what is known as "normal threshold of audibility" has been found. The bearing of threshold of audibility of an average ear on the frequency of a note has been illustrated in fig. 2, below. Audibility is expressed as the effective sound pressure

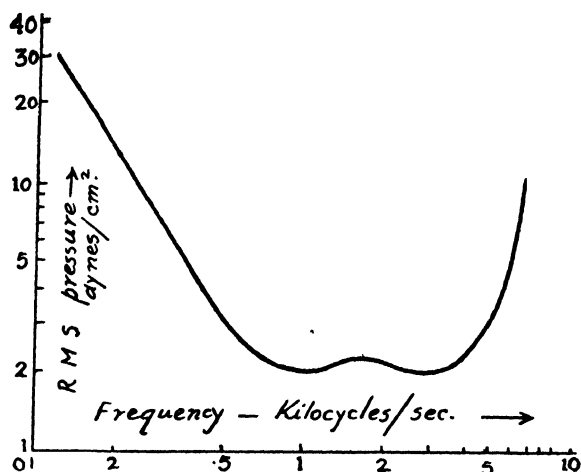


Fig. 2

in a free field. The results expressed in the above figure are due to Churcher, King and Davies⁶ and refer to the condition when the observer is facing the source using both ears. The study of the relation enables one to conclude that the ear is much more sensitive to tones in the middle of the frequency range than to those of the lower or higher pitch. For instance, at a frequency of 1000 cycles per second, a pressure rise of 0.0002 dynes per sq. cm. can be detected by an average ear.

(ii) Limits of audibility :

In fig. 3, are shown the upper and lower limits of the audible sound of various frequencies, the upper limit showing the

threshold of feeling or pain in the ear. The region between these is said to be the accomodation of the ear.

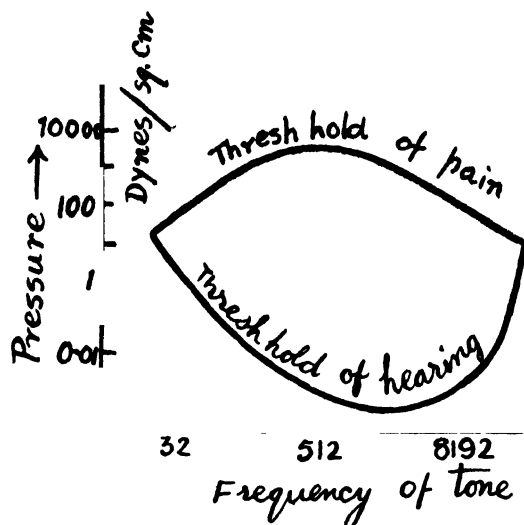


Fig. 3.

(iii) Equal Loudness Curves :

Pressures or intensities are physical data obtainable from instrumental measurements of the sound. They do not convey to us anything beyond the measure of the quantities in physical terms. Sounds which have the same intensity are not usually equally loud, if they are of different pitch. Intensity is an effect of pressure, frequency etc. Loudness is the effect which the pressures have upon human ear. In the following fig. 4., are shown the intensities of sound of different frequencies which are judged to be equally loud by the ear. These relations are based upon the results of Kingsbury⁷. The question now arises as to how loudness is to be measured. For pure tones, this is a simple matter, for loudness is related to physical intensity depending upon the pitch of the tone. For complex tones which approximate to noise, the relation between loudness and physical intensity is extremely complicated. The fundamental method, therefore, of measuring loudness must depend upon the aural observations by normal human observers.

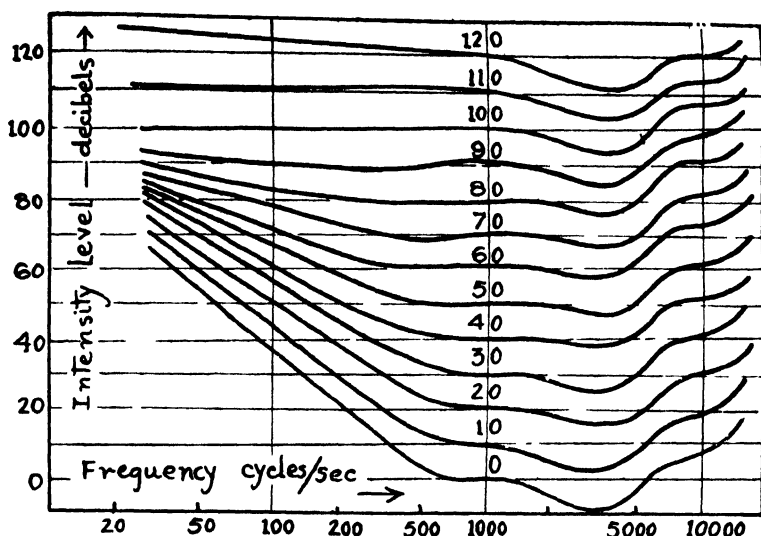


Fig. 4.

(e) The Noise Standard.

(i) Phon :

The process adopted for scientific measurement of noise consists in adopting a standard noise and varying its strength on a scale of energy units until it is judged to be as loud as the unknown noise. This method is akin to estimation of brightness of light by comparing it with a number of standard candles. The noise which has been adopted in England, America and Germany as the standard is a pure tone having a frequency of 1000 cycles per second. With this, all other noises are compared. The procedure for comparison is to listen with both ears alternatively to the test noise and to the standard tone, the standard being adjusted until it is as loud as the test noise. The intensity of the standard is then measured and expressed as so many decibels above the threshold of audibility of 1000-cycle per sec. standard tone. This threshold intensity of a 1000 cycle tone is taken as the fixed zero or datum line and corresponds, as shown already, to an acoustical pressure of 0.0002 dynes per sq. cm. If then the test noise and the standard tone are equally loud and the standard reaches an intensity of n decibels above the threshold, the noise is said to have loudness of n decibels. The term *phon*, however, now replaces decibel to express the loudness of a noise so that "loudness of n decibels" above its threshold

is said to have an "equivalent loudness" of n phons. The meaning of *phon* and equivalent loudness can be further elaborated below.

(ii) Phon and decibel.

It is necessary now to know how noise came to be expressed in terms of 'phons'. We have said above that "loudness of noise is equal to that of standard tone when the tone is operating at n decibels above its zero". This statement led to considerable confusion and ambiguity because noise does not increase by n decibels when its own energy (intensity) increases by n decibels. Davis⁴, therefore, suggested that the term phon should be used to express loudness and decibel limited to express intensity ratios. It should be noted that the number of phons is not proportional to the loudness of noise. It becomes necessary, therefore, to express "equivalent loudness" into numbers proportional to the loudness called "loudness figures". As a convention, if "loudness figure" of 100 is assigned to a noise level of 100 phons and if L is a number proportional to the loudness of a noise, (i.e. L is a loudness figure), then

$$L = (\text{Phons})^4 \cdot 10^{-6}$$

This relation has been shown graphically in fig. 5. It has been

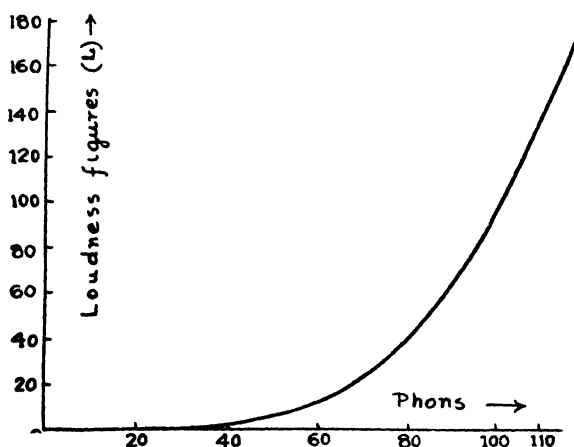


Fig. 5

established by Fletcher and Munson⁽⁸⁾, Ham and Parkinson⁽⁹⁾ and others by finding how the loudness of a 1000-cycle per second

tone varies with its intensity. Thus we can differentiate between the terms "equivalent loudness" and "loudness figure".

The following table is instructive, in that it gives the limits of audibility of the normal human ear.

LIMITS OF AUDIBILITY

Reference standard : 1000 cycle per second tone.

<i>Lower Limit</i>		<i>Upper Limit</i>
(Threshold of hearing)		(Threshold of pain)
Intensity	10^{-16}	10^{-8} watts/sq. cm.
Energy density	2.94×10^{-14}	0.294 ergs/cu. cm.
Pressure R.M.S.	2.04×10^{-4}	645 dynes/sq. cm.
Particle Velocity	4.9×10^{-6}	15.5 cms/sec.
Phons	0	130

(f) Sound Measuring Equipment : Noise meters.

The realisation of the standard scale of "equivalent loudness" involves listening to the test noise and to the standard tone of 1000 cycles per-sec. alternately. Rigorous translation of this procedure into practice is beset with a number of experimental difficulties. Hence this standard method is suitable only for laboratories where elaborate technique is available. In practice, however, we must employ simpler technique. Convenient and compact instruments are now available on the market known as noise-meters. There are two types of these, *viz.*, subjective and objective noise-meters.

(i) Subjective Noise-meters.

One of the earliest forms of a subjective noise-meter is that due to H. Barkhausen. All such meters apply a comparison tone of suitable strength to the ear in some convenient manner. The standard tone is produced in a telephone earpiece by suitable buzzer or oscillator, and is controlled in strength until it is judged by the observer to be as loud as the noise. Such instruments were first used in noise measurements carried out by the National Physical Laboratory. The various forms of the instruments differ in the manner in which the standard tone is applied to the ear. Davis used tuning fork having frequency of 640 vibrations per second as a portable noise-meter. The method he followed was to note the time that elapses before the loudness of the fork falls to the loudness of the observed noise. By adopting this simple method, he measured the noise-levels of various situations.

Usually in a subjective noise-meter, the noise and the standard tone are heard together. This procedure does not give the same results as the standard laboratory technique in which alternate listening to the standard tone and the noise is employed. Modifications are therefore introduced which arrange for the alternate listening. With these meters, masking method can also be employed to take observations. Instead of noting the usual point at which the tone is just as loud as the noise, the masking method observes the point at which the comparison tone is just masked by the test noise, when both are heard together. The masking procedure suffers, however, from many disadvantages and is liable to errors.

(ii) Objective Noise-meters.

The production of such a device depends upon the ability to determine a function of the sound pressures and frequencies which is sufficiently close approximation in magnitude to the resulting sensation of loudness. Although, measurements of loudness are essentially aural in nature, it is desirable to have physical instruments of indicator type on which the readings are in accord with the average aural judgement of equivalent loudness. The method used in objective noise-meters is to feed a microphone output with an amplifier which has a response such that the frequency characteristic is similar to that of human ear, at the specified intensity level. The amplifier frequency response is made variable to suit two or more intensity levels. For complex tones this instrument cannot be made as reliable and precise as it could be for pure tones. Moreover, it takes no account of the subjective tones that would be formed in the ear. For measurement of impulsive noises, the readings obtained with the objective noise meter will be dependent upon the time constants of the circuit and of the meter. By judicious choice of these, this meter may be made satisfactory over various ranges of noises. Steudel⁽¹⁰⁾ has described an objective noise-meter designed specially to deal with impulsive noises. Though convenient in use, this meter is subject to errors and has to be checked against the standard method or against a subjective noise meter serving as a sub-standard.

(iii) Comparison of the Noise-meters.

In comparing the merits of the two types of noise meters described above, it may particularly be noted that subjective noise meter is a small, compact and portable piece of equipment. It

enables the noise to be assessed in a simple and direct manner. On the other hand, the objective noise meter is a bulky and expensive piece of apparatus. But the advantage lies in its being an indicator type of instrument and as such quick to operate and immediately gives a definite and reproducible reading. Such a meter if subjected to appropriate test by a standardising laboratory would not fail to give satisfactory measurements. Such test must necessarily involve its adjustment for impulsive noises. A very satisfactory objective noise-meter was evolved by Davis⁴ both for steady and impulsive kind of noises. It was by this instrument that measurements on "Noise in the operation of mechanically propelled vehicles" were carried out for the British Ministry of Transport at the National Physical Laboratory. The objective type of instrument saves considerable time of the observer and is free from errors depending on personal judgment, which are unavoidable in observations by a subjective noise meter. If, therefore, the question of portability and expense is no consideration, a properly calibrated objective noise meter is certainly to be preferred to a subjective one in point of reliability.

(g) Some noise-levels.

The following are the observations on "equivalent loudness" of various noises in different situations⁽⁴⁾ :

<i>At home</i>	<i>Phons</i>	<i>In restaurant</i>	<i>Phons</i>
Loud radio music	... 80	Loud music	... 90
„ „ speech	... 70	Noisy clatter	... 80
Conversation	... 60	Average music	... 70
Soft radio music	... 50	Moderate clatter	... 60
Clock ticking	... 40	Quiet restaurant	... 50
Quiet garden	... 30		
„ whisper	... 20		

<i>In the street</i>		<i>In vehicles</i>	
Motor horn	... 90	Noisy aeroplane	... 120
Accelerating traffic	... 80	Noisy tram	... 90
Moderate London traffic	70	Quiet aeroplane	... 80
Quiet car passing	... 60	Bus, train, tram	... 70
Quiet street (London)	... 50	Quiet train window closed	60
Quiet suburban street	... 40		

II

ABATEMENT OF NOISE.

In recent years considerable impetus has been given to the measurement of noise by the rapid progress in design of noise-measuring instruments. Several standardised instruments are being placed on the market as a result of specifications being adopted by the American Standards Association, for noise meters of objective type. We can now measure 'decible' with as much ease as we measure volt or ampere. As a consequence, industrial noise measurements are now possible with ease. Sound surveys of buildings, streets, offices, plants etc. with a view to elimination of unwanted noise can be easily planned with convenient and accurate noise measuring equipment.

The problem of the suppression of unwanted noise requires systematic preliminary study of the situation. The situation has to be analysed for (1) the source of noise, (2) the method of transmission and (3) the manner in which the noise is excited. After getting the information on these points, the operator has to read the noise levels and then determine the extent to which the noise has to be suppressed. A systematic procedure of this type gives enough information for the purposes of adopting measures for noise elimination. It is beyond the scope of this short article to deal with the methods used in obtaining the preliminary information necessary for application of noise-elimination technique. It will be a matter for special treatises. In what follows, we shall take a survey of only the methods used in reduction or elimination of noise.

The different ways by which the object of noise abatement can be achieved are (1) avoiding its production, (2) suppressing it at the source, (3) preventing it from being transmitted to the hearers and (4) absorbing it as much as possible if the path itself cannot be adequately blocked. The question of suppression of noise is a matter of public opinion. Much of the noise would cease if those to whom it is due are made aware of the inconvenience caused. There are certain very definite situations in which the production of objectionable noise could easily be avoided, if certain moral codes of society are adhered to. Problem of noise reduction is thus not strictly a technical one. It is a matter for public reaction to something objectionable. There are, however, certain noises which need technical treatment. For instance, in normal civilized life,

the society needs the services of vehicles, factories, technical appliances, etc. These are bound to produce different degrees of noise. It is when they assume unlimited proportions from the point of view of our audibility capacity, that it becomes necessary to think of measures for their suppression. Suppression of noise at the source is dependent upon the study of the source and its various structural details. The types of machines that are in use for various purposes are numerous and they all emit noise to a great or small extent. The need for silencing the machines varies with the circumstances and each machine represents a problem of its own. The essential principle that is to be observed in making these devices produce less noise, is to limit the vibrations to the minimum value by minimising the forces exerted by the numerous moving parts within the machine. In the high-speed machinery the transmission of its resulting vibrations to the walls and floors of building in which it is situated, can be prevented by proper and suitable insulation of the machinery from the foundation or the floor. Then there is the noise from fans and propellers, motor vehicles, trains and trams, air-craft etc. Reduction of it at the source is carried out by adopting measures peculiar to each source and cannot in any way be generalised. In general, in devising means to suppress noise, each detail contributing to the resultant noise effect must be attended to separately.

When the means of suppressing noise at the source to a desired degree become ineffective or are impossible to be adopted, it becomes necessary to take steps to absorb noise during its passage to the hearer. This can be done either by confining noise at the source or by excluding it separately from many points to which it can gain access. The former alternative is to be preferred from the point of economy. Resort to latter would mean application of sound proof materials to each and every situation in the vicinity of the noise-producing source. Thus in a residential district, protection from disturbance of a noisy machinery is obtained by sound proofing the building structure or shelter containing the machinery. Disturbance from everyday noises arising out of the traffic of adjoining roadway, is avoided by having double windows and keeping them closed. This procedure would call for adequate ventilation by mechanical means such as fans and ducts. As a guide to control of noise, the following list of Knudsen, giving tolerable noise levels that can be accepted with confidence, would prove useful :

TOLERABLE NOISE LEVELS

					Phone Limits.
Hospitals	...	...	...	...	15-20
Broadcasting or sound recording studio				...	15-20
Music Studio	...	...	...	...	20-25
Apartments, hotels, homes			...	...	20-30
Auditoriums, libraries	...	...	...	...	20-35
Private offices	...	...	...	...	30-40
Public offices	...	...	...	...	35-40

The above values are based upon the measurement of loudness of noises existing in the background and then inferring how much reduction is necessary to bring the loudness of the given noise to a tolerable limit. In other words, these values take into account the adaptability of normal people to general continuous background of noise. Reduction is caused by either of the methods discussed in this section, but where it is brought about by partitions in the path, the type of these depends upon the characteristics of noise, *i.e.* high-pitched, low-pitched etc.

Concluding Remarks.

It is becoming increasingly evident that public opinion and tendency in the Western Countries is now towards the control of noise. In England, what the Ministry of Transport and local Authorities are doing by way of legal control, the Anti-Noise League is doing by propaganda to prevent unnecessary and inconvenient noises. Breaches of laws are punishable by fines. The Road Traffic Act of 1934, is the manifestation of control relating to the noise of motors and all mechanically propelled vehicles.

Human reactions to noise are varied and many. Investigations so far made have shown that there is close connection between noise and work and noise and deafness. Evidence is fast gathering in favour of noise-reduction, though there are some instances in which the results of test are conflicting. There is no denying the fact that mental efficiency and sharpness are a consequence of elimination of persistently offensive noise. It is unfortunate that in this country, no organised attempt has been made to make the people noise-minded even though we have in India, big cities and industrial towns which can compete with similar places in the West, in respect of the problems of noise. Such detached efforts as have been made so far, are not enough. As a first step in the direction of the control of noise in this

country, noise surveys may be undertaken by Noise Commissions established on the lines of Smoke Nuisances Commissions. Such surveys will, in course of time, accumulate enough data for the purposes of suppression of unwanted noise. Whatever may be the factors controlling noise, one may hope that restriction of noise either by persuasion or regulation will be merely a passing phase and that progress of research will reach a stage when mechanical appliances within specified limits of acceptable noise will be available as remarked by Davis in a recent publication.

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ABSTRACTS OF Ph.D. THESES

I—(1) THE HYDROGENATION OF OILS BY THE CONTINUOUS PROCESS AND (2) THE REFRACTIVE DISPERSION OF GHEES AND VEGETABLE OILS. By V. T. Athavale.

(1) The investigation on the hydrogenation of oils by the continuous process is presented in six parts. Part I contains the description of the apparatus used for the continuous hydrogenation of oils and for the analysis of the hydrogen. An account of the method of preparation and the space-time-yields at various temperatures for (1) the nickel wire, (2) 'Monel' wire, (3) 'Ferry' wire, (4) Raney's catalyst, (5) Nickel carbonate-kieselguhr prepared from nickel sulphate, (7) unsupported nickel carbonate (8) Nickel peroxide—Kieselguhr and (9) Nickel hydroxide—silica gel catalysts in the hydrogenation of groundnut oil is given in Parts I, II, III. The comparative activities of all the above preparations of nickel are given in a tabular form in Part III, which shows that the space-time-yields with an unsupported nickel carbonate catalyst are the highest. The activities of the other catalysts decrease in order: Nickel wire, Monel wire, Nickel carbonate — kieselguhr, Nickel peroxide — kieselguhr. The last two have practically the same activities,

Life tests of the catalysts (1), (5), (8), and (9) showed that the activity in the case of (1) and (9) fell by above 50% in five days, in the case of (8) to about 40% in seven days while in the case of (5) a periodic rise and fall in the activity was observed, and the activity did not drop below 75% even after ten days continuous run. The preparation of (8) was inconvenient. It appeared that the kieselguhr—carbonate which is known to be the best catalyst in a batch process is the best catalyst in the continuous process also.

The design of semi-commercial plants capable of yielding 4 cwts. and one ton oil per day of ghee consistency is described in Part III and the trial experiments with precipitated catalysts were quite successful.

Part IV deals with the hydrogenation of olive and cottonseed oils by Kieselguhr-nickel carbonate catalysts. Measurements of the space-time-yields at different temperatures showed a regular change in the behaviour of the catalyst depending on the composition of the oil hydrogenated. Analysis of the hardened cottonseed oil indicated a selective hydrogenation of olein at 150°.

In all the above cases the apparent velocity coefficients of the reaction were calculated

by the formula $K = \frac{2.3}{t} \log \frac{a}{a-x}$

which gave concordant values for K in the case of nickel wire catalyst at 140°—180° and in the case of silica gel-nickel hydroxide catalyst at 100°, 160° and 200°. In the case of other catalysts and the oils, the values differed with rates of the flow of oil over the catalyst, and this variation could be expressed by an adsorption equation $K = K' e^{1/T}$ which gave concordant values for K' at all temperatures. The corrected velocity coefficients when plotted against temperature showed that the reaction velocity was high at two temperatures 150° and above 200°, the high reaction velocity at the former temperature being selective towards the hydrogenation of olein.

In order to verify the above conclusions, the hydrogenation of a pure substance like ethyl oleate was taken up and an account of the same is given in Part V. The measurements of iodine values, refractive indices and dispersions of the hydrogenated products were carried out which showed that the iodine value varied linearly with refractive index only after the former had dropped down by about 25 %, the variation of the refractive index with iodine values in the initial stages being comparatively greater. The dispersions of the hydrogenated products showed a considerable difference in the samples having either the same refractive index or the iodine value, and depended

on the temperature at which the samples were hydrogenated, a marked deviation being observed in the case of samples hydrogenated at low temperatures. It was concluded that there are isomers of oleic acid formed in the reaction, the lead soaps of which are soluble in ether. The marked variation in the dispersion at low temperatures was because of the formation of these isomers due to the low activity of the catalysts for hydrogenation at these temperatures.

The hydrogenation of ethyl oleate confirmed the findings in the case of oils in that a high reaction was observed at 150° and 200°.

The mechanism of the continuous hydrogenation of oils is discussed in Part VI. A brief survey of the literature on the mechanism and kinetics of hydrogenation is given. From various considerations it has been shown that the catalytic hydrogenation is a sum of three factors, viz. (1) Activated adsorption of hydrogen which decreased very slowly from 100°–200°, (2) Selective adsorption of olein by monovalent nickel. The adsorption becomes appreciable above 125° and increases rapidly up to 150°–160° and decreases gradually at higher temperatures, and (3) adsorption of both olein and linolein by divalent nickel. The adsorption is appreciable even below 100° and increases gradually to a maximum at about 240°C.

These results have been used to explain the selectivity in the hydrogenation of oils and the other peculiarities observed during the course of investigation.

(2) REFRACTIVE DISPERSION OF GHEES AND VEGETABLE OILS :

This investigation was carried out with a view to see whether the measurement of the dispersion of ghees can be used for characterising its purity and to detect if possible the adulteration with oils. The refractive dispersions of genuine ghees from Sindhi cow, Jersey cow and Indian buffalo and of groundnut, safflower and olive oils were measured at 40° on a Pulfrich refractometer, and it has been shown that the dispersion constants in the case of oils and ghees are different. The previous results of Fryer and Weston and others on the refractive dispersions of oils, fats and fatty acids have been recalculated, and it is concluded that the measurements of the refractive dispersion can be successfully used to detect the adulteration of butter-fat.

S. K. K. J.

II—(A) ACTIVATION AND CLARIFYING. PROPERTIES OF FULLER'S EARTH. By B. S. Kulkarni, Indian Institute of Science, Bangalore.

Part I: A brief account of the general properties of Fuller's

*Earth and its production, particularly in India, is given:—*The author has also examined the various theories which have been put forward to explain the activation and bleaching properties of the earth into three main groups, viz., (1) theories giving prominence to chemical composition of the earth, (2) theories of adsorption and the recently suggested theory of the zeolitic nature of the earth, based on its structural composition. While adsorption may play an important part in bleaching action, what is responsible for both activation and clarification is the behaviour of the earth as hydrogen zeolite.

*Part II: The Decolorising Action of some Indian Fuller's Earths:—*Indian Fuller's earths have been examined with regard to their bleaching properties and the hydrogen zeolite content, and compared with two well known foreign earths.

It has been shown that the hydrogen zeolite content of the earths is mainly responsible for decolorisation.

*Part III: Bleaching of Safflower oil by Fuller's Earths:—*Further evidence has been brought forward in support of the hydrogen zeolite theory of decolorisation of oils by fuller's earth using safflower oil and earths treated in different ways.

Calcium and aluminium earths were inferior in bleaching action. Activated earths are deactivated when treated with alkalies.

It has been shown that one of the Indian fuller's earths could be activated by subjecting its suspension to electrolysis.

Part IV: Equilibrium in the Ionic Exchanges in Fuller's Earth:—The limit of hydrogen ion exchange ability by sodium ion in fuller's earth has been measured by potentiometric methods in concentrated solutions and conductivity method in dilute solutions of sodium chloride. Concordant results were obtained for the value of the equilibrium constant for the base-exchange reaction in the latter experiments. The effects due to adsorption were minimised by rejecting the colloidal portions of the earth.

A similar limit was found in the decolorisation of a vegetable oil using different amounts of fuller's earth.

The value of the equilibrium constant obtained for the exchange of sodium ion by hydrogen ion shows that the latter even in small concentrations should be most effective in replacing other ions. In actual practice, acid of high concentrations is employed for activation as it breaks up the fuller's earth and thereby increases the effective surface.

Part V: Dehydration of Fuller's Earth:—The identity of the mineralogical constituent of some Indian fuller's earths, with montmorillonite, has been established by a study of the comparative dehydration curves.

The difference between the kaolinitic clays and those of the montmorillonite group, is shown by the different types of water given out during dehydration.

The hydrogen exchange capacities of the earths are maximum when dehydrated between 150–200°, the activity being destroyed at higher temperatures.

The decolorising power of the various earths is also maximum when heated at 150–200°, and is found to be inversely proportional to pH, in agreement with the results obtained previously. It appears that the decolorising action of fuller's earth is due to adsorption by hydrogen zeolite.

Part VI: Adsorption of Colouring matter by Fuller's Earth in Decolorisation of oils:—A systematic study of the problem of removal of the colouring matter in vegetable oil by various Indian earths has been made and the results have been examined in light of the Freundlich isotherm.

It is found that although the relationship between the colour-removed X and the colour-remaining C appear to follow exponential curves, the various requirements of the Freundlich isotherm are not fulfilled.

The process of colour removal follows Freundlich law only over a very limited range of concentrations. The law appears to break down for higher and lower concentrations of the colouring matter and for higher

concentrations of the highly active earth and low concentrations of the low grade earths.

It is suggested that although some of the colouring matter is removed by purely physical adsorption, the remaining probably forms definite chemical combinations with hydrogen of the earth and remains attached to the surface. Many previous observations strongly support the view of decolorisation of oils.

(B) THE MECHANISM OF THE COAGULATION OF COLLOIDAL SOLUTIONS.

Part I: Arsenious Sulphide Sol.—The electrical conductivity of As_2S_3 sols increases slowly in the dark, but more rapidly when exposed to light. This is attributed to a chemical reaction, which is accelerated by light.

The total conductivity of the As_2S_3 sol increases on dilution probably owing to a liberation of adsorbed arsenious acid from the particles.

On the addition of small quantities of coagulating electrolytes, to As_2S_3 sols, the conductivity decreases in the dark slowly in the case of KCl, but much more rapidly in the case of $BaCl_2$ and $FeCl_3$, long before there is any trace of coagulation. The variation in conductivity with time is gradual and never abrupt.

The observed conductivity of the 'sol-electrolyte mixture is distinctly less than the calculated one.

An ultramicroscopic examination of the coagulating sol shows that the particles gradually form groups, which grow in size, and also sometimes strings of adhering particles.

An explanation for the observed changes in the conductivity is suggested, and a view of the mechanism of coagulation is given, based on the author's own observations and those of other workers, particularly, of Weiser.

Part II: Ferric Hydroxide Sol.—The electrical conductivity of the ferric oxide sols is quite constant and is not altered on exposing the sol to light.

The total conductivity of the Fe_2O_3 sol increases on dilution, probably owing to the liberation of the adsorbed ferric chloride, which is then hydrolysed.

On the addition of small quantities of coagulating electrolytes, *e.g.* potassium sulphate to the Fe_2O_3 sols, the conductivity decreases very rapidly during the first minute or so after addition, and then shows a very slow decrease. When potassium chloride is added a slight initial increase in conductivity is noticed; and later on it decreases slowly.

An explanation for the observed changes in conductivity is suggested, and a view of the mechanism of coagulation of Fe_2O_3 sols by multivalent ion like the sulphate ion and by chloride ions is given.

Part III: Mutual Coagulation of Sols.—The process of coagulation between the positively charged Fe_2O_3 sol and the negatively charged As_2S_3 sol in complete darkness and when exposed to daylight has been studied by following the conductivity changes during the process.

The results suggest that mutual coagulation of the two sols is not due to the interaction between the stabilising ions in the two sols, or the neutralisation of the positive and negative charges. The following mechanism appears to be very probable: on mixing the two sols the opposite charges on their particles help in drawing them into close association, then directly some of the ferric ions adsorbed by the ferric oxide particles act on the As_2S_3 particles, and by a process of exchange adsorption cause a lowering of the charge and therefore decrease in stability of both the As_2S_3 and Fe_2O_3 particles.

In the mutual coagulation of the positively and negatively charged ferric oxide sols, there appears to be an optimum ratio of the quantities of the two sols for the coagulation to become complete. The results suggest that the flocculation in this case is not caused by neutralisation of the charges but by ionic actions. Further work is necessary to know its exact nature.

(C) DETERGENT ACTION OF SOAPS.

Part I: Interfacial Tensions of pure Soap Solutions.—Interfacial tensions against benzene, of aqueous solutions of sodium and potassium soaps of the homologous series are measured and the results compared with corresponding surface tension measurements by other workers.

The results are discussed in the light of the previous theories on the subject and explanations are given for the maximum activity shown by the myristate, and for the increased activity due to unsaturation, presence of hydroxyl group and replacement of sodium by potassium in the soap molecule.

The various units participating in the soap solution equilibria, appear to possess surface activity to a smaller or greater extent; the simple ions of the soaps of the lower series due to their higher osmotic activity, and the aggregated particles of the higher series of fatty acids, due to their less sensitivity to the surface forces, appear to be less surface active than the simple molecules. As these are entirely dissociated, it would appear that the surface activity is mainly dependent upon the nature of the anions. As the latter get concentrated at the surface the cations form a double layer with oriented anions. The difference between the surface activity of sodium, potassium and even

amonium and lithium soaps observed by different workers, thus appears to be due to the fact that the entire soap molecule gets concentrated at the interface.

S. K. K. J.

III—ATTEMPTS TO MAKE OUT THE MECHANISM OF CHEMICAL REACTION: ACTION OF CHARCOAL ON POTASSIUM NITRATE. By T. M. Oza, M.Sc.

With a view to throw light on the reactions involved in the explosion of gunpowder the action of charcoal on potassium nitrate has been studied in detail. The work has been divided into five sections as under :—

Part I. The Interaction between Potassium nitrate and Charcoal.

Section I. Effect of temperature, time, pressure of the evolved gas, mass of potassium nitrate etc.

Section II. A detailed study of the production of flash.

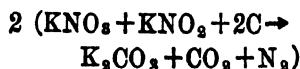
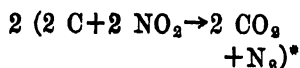
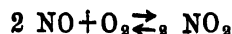
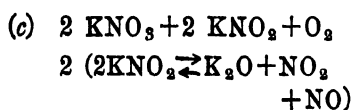
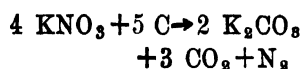
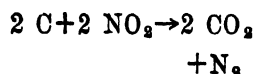
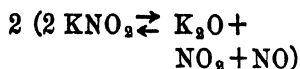
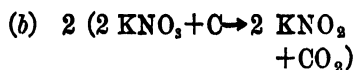
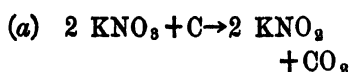
Part II. The Interaction between Potassium nitrite and Charcoal.

Section III. Isolation and Thermal Decomposition of Potassium nitrite.

Section IV. The Interaction between Potassium nitrite and Charcoal.

Part III. Section V. The Interaction between mixtures of Potassium nitrate, Potassium nitrite and Charcoal.

From the results obtained, the mechanism of (a) initial, (b) smooth and (c) violent stages of the interaction between Potassium nitrate and Charcoal has been discussed and represented as shown below :—



* This involves the intermediate formation and oxidation of carbon monoxide leading to the production of a flash.

ABSTRACTS OF M.Sc. THESES

I—STUDIES IN ADSORPTION OF NAPHTHOL DYES BY COTTON FIBRE. By J. A. Nabar, Wilson College, Bombay.

Adsorption of some dyestuffs of the Naphthol AS series by Cotton fibre has been studied in the presence of Alcohol, Sodium Hydroxide, Sodium Chloride, Sodium Sulphate, Sodium Phosphate, Soap, Gum Tragacanth and Agar agar and at different temperatures to understand the mechanism of the process of dyeing.

It is observed that Adsorption of the dyestuffs decreases with increasing amounts of alcohol, Gum Tragacanth and Agar Agar, while it first increases, reaches a maximum and then decreases on adding increasing amounts of NaOH, NaCl, Na_2SO_4 , Na_3PO_4 and soap solutions. Regarding the effect of temperature on adsorption, it is found that (1) the rate of adsorption is greater at higher than at lower temperatures, (2) the equilibrium adsorption increases with the rise of temperature and (3) the amount of increase of adsorption for a particular range of temperature is greater at lower than at higher temperatures.

The results obtained become easily intelligible if it is assumed that the dye particles exist in

colloidal condition and the process of dyeing is interpreted from that point of view.

P. M. B.

II—POTENTIOMETRIC TITRATIONS. By C. T. Abichandani, Indian Institute of Science, Bangalore.

The behaviour of polished tungsten and molybdenum wire electrodes has been studied over a pH range 2–12 in an atmosphere of hydrogen. It has been shown that tungsten electrode gives a theoretical relationship of pH and E.M.F. over a range of pH 2.8–9.4, while molybdenum, over a short range from pH 5 to 7.

Experiments have also been made in an atmosphere of air and oxygen, when the electrodes deviated very much from the theoretical relationship.

Temperature coefficient of the system $\text{Pt}; \text{H}_2$ solution pH WxOy W has been measured and the values for free energy and heat of formation of various oxides calculated. The calculated data agree well with the heat of formation of tungsten trioxide on the surface of the metal.

The tungsten electrode has been utilised for differential titrations using a simple ther-

mionic valve circuit for measurements. The graphs resemble very closely the graphs $\Delta E/\Delta$ c.c. *vs.* c.c. obtained from the direct potentiometric titrations. The method is found to be very sensitive for obtaining end points accurately, and for indicating irregularities in the titration reaction, and has been used by the author for the electrometric titrations of tannic acids from myrobalan and yielded sharp end points in the regions where hydrogen electrode was sluggish and insensitive.

In the case of dibasic acids the differential method shows double peaks and negative inflections at half and full neutralisation points respectively. The former are due to the formation of di-salt before half the acid is neutralised, and the latter is due to hydrolysis.

An automatic apparatus has been developed for potentiometric titrations. A Cambridge curve tracer was used as recording device. The drum of the curve tracer, while rotating, released the sinker in the burette and displaced the standard alkali solution cell. The E. M. F. between the two electrodes increased, which caused an increasing deflection of the galvanometer. The movement of the spot of light was followed by the pointer attached to the recording pen, and the curve traced on the graph paper wrapped round the drum. The approach of the end point was marked by a sudden increase

in the deflection of the galvanometer.

The primary and secondary dissociation constants of *cis* and *trans* caronic, *cis* and *trans* norpinic acids have been measured from the potentiometric titration data. The range over which the two acid groups titrate simultaneously is found to be 70 % in the case of *cis* acid and 75 % in *trans* acids.

The potentiometric titrations of *ortho*-, *meta*-, and *para*-hydroxy benzenes by 0.1 N sodium hydroxide, have been carried out, and the primary and secondary dissociation constants calculated. Correction for interionic attractions have been applied with the help of Debye-Hückel theory. The values of the first dissociation constants for some of the phenols are of the same order as obtained by Euler and Bolin. The second dissociation constants for all the substances have been determined for the first time. In the case of phloroglucinol both the OH groups titrate simultaneously, as the two dissociation constants are of the same order. The first and second dissociation constants of pyrogallol and phloroglucinol have been determined for the first time.

The effect of distance between the two ionising groups on the dissociation constants is shown, not only by the marked change in the first dissociation constants but also more prominently by the

ratio K_1^a / K_2^a . The order of the first dissociation constants is $o > m > H > p$ in the benzoic acids, and phloroglucinol > pyrogallol > catechol > resorcinol > hydroquinone in hydroxy benzenes. The order of the second dissociation constants of the benzoic acids is the reverse of that of the first dissociation constants.

A straight line relationship has been shown to exist between the $\log K_1^a / K_2^a$ and the molar absorption coefficient in the infra-red region at 7000 cm^{-1} , for phenols. In catechol and pyrogallol the extinction of the band at 7050 cm^{-1} is accompanied by the appearance of a decreased frequency at 6970 cm^{-1} which is due to the weak OH bond responsible for the increased first dissociation constant.

S. K. K. J.

III—(1) UTILISATION OF MYROBALANS, (2) POTENTIOMETRIC TITRATIONS OF TANNIC ACIDS. By S. R. Sunthakar, Indian Institute of Science, Bangalore. .

Part I

Chapter I contains analysis of myrobalans by (a) hide powder method and (b) volumetric method with potassium permanganate; and extraction of myrobalans with water on laboratory scale. Optimum con-

ditions regarding time and temperature of the extraction and the quantity of water to be used for the efficient extraction are determined. Cooling the myrobalan extract from room temperature 25°C to 5°C shows that it is desirable to cool the same to 15°C , as it improves the colour and the ratio of tannin to non-tannins without appreciably affecting the yield. In order to estimate quickly and fairly accurately the total soluble matter contained in the myrobalan extracts obtained in the successive leachings, the relation between (a) Sp. Gr. and temperature, and (b) Sp. Gr. and percentage of soluble matter in the extract are determined, which show linear variations of Sp. Gr. both with temperature and percentage solubles. In decolorisation of the myrobalan extract with alumina cream, it is found that the ratio of tannin to non-tannins goes on decreasing progressively as the quantity of alumina cream added goes on increasing, obviously due to the formation of aluminium tannate.

Chapter II deals with preparation of myrobalan extract on large scale. The simple laboratory vacuum climbing and falling film evaporator is described.

In chapter III purification of tannic acid from myrobalans by fractional precipitation with lead acetate is described. The results show that a minimum quantity

of lead acetate solution should be added in the first fraction, which is to be rejected, and which precipitates more non-tannins than tannins. In the middle fraction proportionately more non-tannins are precipitated than tannins with increasing quantities of lead acetate solution.

Chapters IV and V deal with the utility of myrobalans in ink manufacture and in cotton dyeing as mordant. Different samples of inks with varying quantities of gallotannic acid, myrobalan extract, myrobalan tannic acid and E. Merck's commercial tannic acid were prepared and were tested for their stability to form sediment. Washing and fading tests were carried out with water and alcohol. In order to judge their corrosive action, the conductivities of the inks were determined with the Leeds and Northrup apparatus. For comparison four commercial inks were taken, (1) Stephen's Blue Black writing fluid, (2) Swan Blue Black ink for fountain pens, (3) Quink ink made by Parker Pens, Ltd., (4) Inkotine, manufactured by G. S. Ranade, Bombay. The mordanting power of extract and tannic acid prepared from myrobalans is compared with that of the commercial tannic acid manufactured by E. Merck. It can compete very well in medium and heavy shades of basic colours, but in light shades the yellow colour of the myrobalans interferes.

Chapter VI deals with myrobalan oil. In the present investigation physical and chemical constants of the myrobalan oil and of the liquid unsaturated and solid saturated fatty acids from the oil are determined. The composition of the liquid unsaturated acids approaches that of the pea-nut oil.

Part II

The first dissociation constants of chebulinic, ellagic and ellagitannic acids have been determined by the potentiometric method, and it has been shown that ellagitannic acid from myrobalans is nearly as strong as gallic acid.

The various tannic acids have been electrometrically titrated by the differential method, and the equivalents and the polybasic nature of these acids have been confirmed.

The significance of the pH of the various solutions of myrobalan tannic acids from the point of view of tanning has been pointed out.

All the tannic acids showed prominent spurious peaks in the differential titration curves for which no adequate reason could be assigned. Importance was given to those equivalents which were confirmed by the appearance of subsidiary peaks which were multiples of the main peak.

The quarter basic nature of chebulinic acid and the value of the equivalent have been

found to be in accordance with the original digalloyl structure of this acid given by Freudenberg and Fick with, however, six molecules of water of crystallisation.

Ellagic acid was titrated to the second stage of neutralisation. The equivalent was found to be in agreement with the original formula suggested by Schiff.

The electrometric titration of ellagitannic acid shows the first stage of neutralisation corresponding to the formula $C_{26}H_{22}O_{19}$ (Nierenstein) and the last stage being shown when the value of the equivalent is $1/5$ of the first, these results being in agreement with the fact that there are four hydroxyl groups and one carboxyl group in the acid, the intermediate stages of neutralisation being also indicated by subsidiary peaks.

The first and second dissocia-

tion constants (4.6×10^{-5} , 2.57×10^{-6}) of gallic acid have been determined, corresponding to the dissociation of the carboxyl and that of one of the phenolic groups which is stronger than the remaining two. The quarter-basic nature of this acid has been clearly shown although the dissociation constants for the other stages were not calculated.

In the case of gallotannic acid the first dissociation constant (1.32×10^{-5}) has been calculated, the equivalent found being in agreement with Nierenstein's formula when $x=3$. The remarkably high value of the dissociation constant is obviously due to the acid obtained by the easy hydrolysis of the lactone, which is the distinctive feature of Nierenstein's formula "polydigalloylencodigallic acid anhydride".

S. K. K. J.

SCIENCE NOTES

A NOTE ON THE CALCULATION OF THE INTENSITIES OF LIGHT SCATTERED ON SPHERICAL OBSTACLES.

By

G. R. PARANJPE AND S. S. LAJMI

The problem of scattering of light by a particle has been worked out by Rayleigh,¹ Mie² and others. The theory of Rayleigh involves the assumption that the spheres, if large as compared with the wave-length, has optical properties little different from these of the surrounding medium. The theory of Mie does not suffer from any such assumption and is valid for spheres of any size and any material. The extremely large amount of numerical work necessarily limits the usefulness of the theories to fairly small spheres. Using the method employed by Blummer³, it has been possible to extend the verification of Mie's theory to considerably larger particles and in all directions. The object of the present note is to describe in detail the numerical evaluation of the different intermediate terms for the final expressions of intensity.

Mie calculates the amplitudes of the waves of light radiated by the particle in various directions. The equations include a series of partial waves into which the total radiation is divided. When a beam of unpolarized light is incident on a particle, Blumer expresses the intensities of scattered light, (i) J_1 polarized in the horizontal plane containing the observed scattered light and the incident beam and (ii) J_2 polarized in the vertical plane, as follows :—

$$J_1 = \frac{\lambda^2}{4\pi^2 r^2} \left| \sum_{n=1}^{\infty} \left\{ A_n \pi_n + P_n [\pi_n v - \pi'_n (1 - v^2)] \right\} \right|^2$$

$$J_2 = \frac{\lambda^2}{4\pi^2 r^2} \left| \sum_{n=1}^{\infty} \left\{ A_n [\pi_n v - \pi'_n (1 - v^2)] + P_n \pi_n \right\} \right|^2$$

¹ In the paper by G. R. Paranjpe, Y. G. Naik and P. B. Vaidya published in the Proc. Ind. Acad. Sc. Vol. IX, 1939, p. 335, the symbol μ is used instead of v .

The factor $\frac{\lambda^2}{4\pi^2 r^2}$ is a constant for a given value of λ , the wave-length of incident light, and r the distance of the observer from the particle. (This distance is of importance in the experimental determination of the size of the particle, using the corona ring method). This factor can, therefore, be omitted from numerical evaluation of intensities of scattered light in a given set of conditions. It is assumed that $r \gg \varrho$, where ϱ is the radius of the particle. Thus—

$$J_1 = \frac{\lambda^2}{4\pi^2 r^2} \cdot I_1$$

$$J_2 = \frac{\lambda^2}{4\pi^2 r^2} \cdot I_2.$$

where I_1 and I_2 will be proportional to the intensities of scattered light in the horizontal and in the vertical planes. In the expressions, given above, n is the serial number of a partial wave of the scattered light and $\nu = \cos \vartheta$, where $(\pi - \vartheta)$ is the angle between the incident beam of light and the direction along which the intensity of scattered light is to be calculated. The symbol $| \cdot |^2$ indicates that the square of the absolute value in the parenthesis is taken.

A_n and P_n are complex functions depending on the wave-length of light λ , the radius of the particle ϱ and the refractive index m' of the material of the particle with respect to the surrounding medium.

$$A_n = \frac{(-1)^n(2n+1)}{n(n+1)}.$$

$$\frac{\beta \cdot S'_n(\alpha) \cdot S_n(\beta) - \alpha \cdot S_n(\alpha) \cdot S'_n(\beta)}{\{\beta \cdot S_n(\beta) C'_n(\alpha) - \alpha S'_n(\beta) C_n(\alpha)\} - i\{\beta \cdot S'_n(\alpha) S_n(\beta) - \alpha S_n(\alpha) S'_n(\beta)\}}$$

$$P_n = \frac{(-1)^n(2n+1)}{n(n+1)}.$$

$$\frac{\beta \cdot S_n(\alpha) S'_n(\beta) - \alpha S'_n(\alpha) \cdot S_n(\beta)}{\{\beta S'_n(\beta) \cdot C_n(\alpha) - \alpha S_n(\beta) C'_n(\alpha)\} - i\{\beta S_n(\alpha) S'_n(\beta) - \alpha S'_n(\alpha) S_n(\beta)\}}$$

where $\alpha = \frac{2\pi\varrho}{\lambda}$ and $\beta = m' \cdot \alpha$.

The functions $S_n(\alpha)$, $C_n(\alpha)$ and $S_n(\beta)$ are of the form $S_n(x)$ and $C_n(x)$, which are solutions of the differential equation

$$\frac{d^2}{dx^2} (U_n) + \left\{ 1 - \frac{n(n+1)}{x^2} \right\} U_n = 0.$$

So that—

$$S_n(x) = x^{n+1} \left(-\frac{1}{x} \cdot \frac{d}{dx} \right)^n \frac{\sin x}{x}; \quad S_n^1(x) = \frac{d}{dx} S_n(x)$$

$$C_n(x) = x^{n+1} \left(-\frac{1}{x} \cdot \frac{d}{dx} \right)^n \frac{\cos x}{x}; \quad C_n^1(x) = \frac{d}{dx} C_n(x).$$

Putting in the values of n ,

$$S_0(x) = \sin x; \quad S'_0(x) = \cos x.$$

$$S_1(x) = \frac{\sin x}{x} - \cos x; \quad S'_1(x) = \frac{\cos x}{x} + \sin x \left(1 - \frac{1}{x^2} \right).$$

The following recurrence formulæ which are derived from the differential equations given above are used for $n > 1$.

$$S_{n+1}(x) = \frac{2n+1}{x} S_n(x) - S_{n-1}(x) \quad \dots \quad \dots \quad \dots (a)$$

$$S'_n(x) = \frac{n+1}{2n+1} S_{n-1}(x) - \frac{n}{2n+1} S_{n+1}(x) \quad \dots \quad \dots (b)$$

$$S'_n(x) = S_{n-1}(x) - \frac{n}{x} S_n(x) \quad \dots \quad \dots \quad \dots (c)$$

Any one of the above can be derived from the other two. Thus, if from numerical values obtained for $S_n(x)$ and $S_{n-1}(x)$ the value of $S_{n+1}(x)$ is correctly obtained, the two values obtained for $S'_n(x)$ by using (b) and (c) must be equal. If they are not equal, the calculation is to be revised. The recurrence formulæ for $C_n(x)$ and $C'_n(x)$ are similar to the above formulæ for $S_n(x)$ and $S'_n(x)$.

It is again a matter of interest from numerical results that for integral positive values of x

$$S'_{x-1}(x) = S'_x(x) \quad \text{and} \quad C'_{x-1}(x) = C'_x(x).$$

The values of $\sin x$ and $\cos x$ are obtained correct to ten places of decimals from tables given in B.A. Reports, 1916 (p. 60 et. seq.), by the use of Taylor's theorem.

Having calculated $S_n(\alpha)$, $S'_n(\alpha)$, $C_n(\alpha)$, $C'_n(\alpha)$, $S_n(\beta)$ and $S'_n(\beta)$, for a sufficiently large value of n , such that $S_n(\alpha)$ and others become very small, and also having calculated the values of the factor $\frac{(-1)^{n+1}(2n+1)}{n(n+1)}$, we can proceed to evaluate A_n and P_n as

follows :—

$$\begin{aligned}\text{Let } X_n &= \beta \cdot S'_n(\alpha) \cdot S_n(\beta) - \alpha \cdot S_n(\alpha) \cdot S'_n(\beta), \\ X_n^1 &= \beta \cdot S_n(\beta) \cdot C'_n(\alpha) - \alpha \cdot S'_n(\beta) \cdot C_n(\alpha)\end{aligned}$$

$$Y_n = \beta \cdot S_n(\alpha) \cdot S'_n(\beta) - \alpha \cdot S'_n(\alpha) \cdot S_n(\beta)$$

$$Y_n^1 = \beta \cdot S'_n(\beta) \cdot C_n(\alpha) - \alpha \cdot S_n(\beta) \cdot C'_n(\alpha)$$

$$\text{and } K_n = \frac{(-1)^{n+1}(2n+1)}{n(n+1)}.$$

By rationalizing the denominators we get the following values of A_n and P_n :

$$A_n = K_n \left\{ \frac{X_n X'_n}{X_n^2 + X_n'^2} + i \frac{X_n^2}{X_n^2 + X_n'^2} \right\}$$

$$P_n = K_n \left\{ \frac{Y_n Y'_n}{Y_n^2 + Y_n'^2} + i \frac{Y_n^2}{Y_n^2 + Y_n'^2} \right\}$$

The values of the real and imaginary parts of A_n and P_n are shown in the accompanying table I, as a specimen, for $\alpha=12$, $\beta=16$ worked up to $n=18$.

2

The function π_n is the solution of the differential equation

$$\frac{d^2}{dv^2} \left\{ (1-v^2)\pi_n \right\} + n(n+1)\pi_n = 0$$

$$\text{and } \pi'_n = \frac{d}{dv}(\pi_n).$$

For $n=1, 2, 3$, we have

$$\pi_1 = 1, \quad \pi'_1 = 0$$

$$\pi_2 = 3v, \quad \pi'_2 = 3$$

$$\pi_3 = \frac{15}{2}v^3 - \frac{3}{2}, \quad \pi'_3 = 15v.$$

For $n > 3$ we can use the recurrence formulæ obtained from the differential equations which give

$$\pi_{(n+1)} = \frac{2n+1}{n} \pi_n - \frac{n+1}{n} \pi_{(n-1)}$$

$$\pi'_{(n+1)} = (2n-1)\pi_n + \pi'_{(n-1)}.$$

The factor $\{v\pi_n - (1-v^2)\pi'_n\}$ can be calculated from the values of π_n and π'_n obtained as above.

TABLE I

$$\alpha=12, \beta=16 \quad \therefore m^\circ=1.33$$

A_n			P_n	
real part	imaginary part.	n	real part	imaginary part.
0.748558	-0.703519	1	-0.713230	0.981962
-0.408988	0.496291	2	0.402914	-0.310504
0.272949	-0.188863	3	-0.286022	0.348773
-0.224710	0.213615	4	0.185824	-0.098135
0.144746	-0.070819	5	-0.174269	0.126400
-0.105699	0.041717	6	0.113415	-0.049461
0.075918	-0.023596	7	-0.021464	0.001731
0.007721	0.000253	8	0.047831	-0.010168
-0.054984	-0.015452	9	0.045845	0.010476
0.086570	0.055241	10	-0.095450	-0.096384
-0.087100	-0.089019	11	0.087009	0.082701
0.050564	0.142287	12	-0.080072	-0.083112
0.050949	-0.020266	13	-0.063350	0.035905
-0.007876	0.000451	14	0.006180	-0.000277
0.001294	-0.000013	15	-0.000791	0.000005
-0.000202		16	0.000102	
0.000029		17	-0.000012	
-0.000004		18	0.000001	

TABLE II

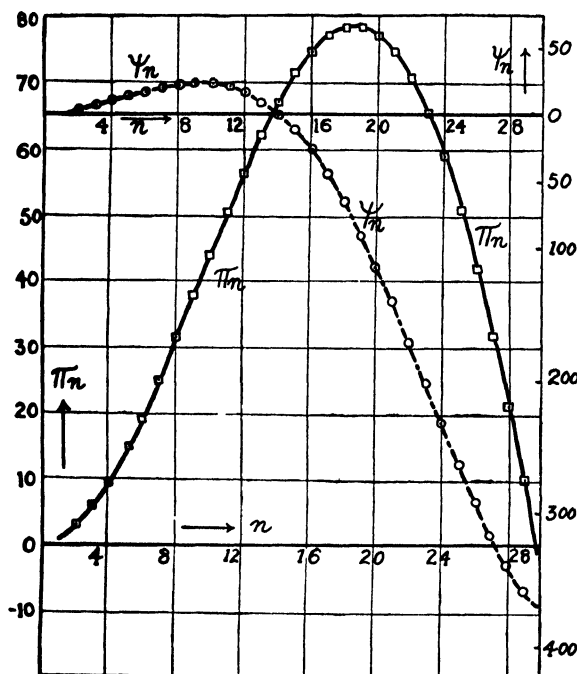
$$Q=7^{\circ}-15^1$$

$$\nu=0.992$$

π_n	n	$\psi_n = \nu\pi_n - 1 - \nu^2\pi'_n$
1.0000	1	0.9920
2.9760	2	2.9044
5.8805	3	5.5963
9.6434	4	8.8624
14.1734	5	12.4398
19.3599	6	16.0167
25.0753	7	19.2437
31.1773	8	21.7456
37.5121	9	23.1247
43.9172	10	23.0255
50.2250	11	21.0488
56.2661	12	16.8667
61.8728	13	10.1870
66.8828	14	00.7764
71.1424	15	- 11.5271
74.5096	16	- 26.8033
76.8579	17	- 45.0410
78.0785	18	- 66.1313
78.0829	19	- 89.8650
76.8053	20	- 115.9231
74.2043	21	- 143.8937
70.2638	22	- 173.2606
64.9945	23	- 203.4174
58.4336	24	- 233.6765
50.6449	25	- 263.2810
41.7181	26	- 291.4193
31.7676	27	- 317.2426
20.9309	28	- 339.8838
9.3663	29	- 358.4773
- 2.7495	30	- 372.1812

The accompanying table II gives the values of the factors π_n and ψ_n , where $\psi_n = v\pi_n - (1-v^2)\pi'_n$. The values are worked out, as a specimen, for $v=0.992$ which corresponds to $\delta = 7^\circ 15'$ worked upto $n=30$. The value are also graphically represented in Fig. 1.

Fig. 1



Curves showing the relationship between π_n and n and ψ_n and n

For $v=1$ or $\arccos v=0$

$$\pi_n = \frac{n(n+1)}{2} = \psi_n$$

For negative value of v , π_n and ψ_n can be obtained as follows :—

$$\pi_n(-v) = (-1)^{n+1} \pi_n(v)$$

$$(-v)\pi_n(-v) - (1-v^2)\pi'_n(-v) = (-1)^n \{v\pi_n(v) - (1-v^2)\pi'_n(v)\}$$

or

$$\psi_n(-v) = (-1)^n \psi_n(v).$$

3

Knowing K_n , A_n , P_n , π_n and ψ_n and substituting them in expressions for I_1 and I_2 , the next step is to obtain the sum of the squares of the real and imaginary parts.

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A VALVE MILLIVOLTMETER WITH RETRO-ACTION.

By

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The following circuit will be found to be useful to measure small voltages of the order of a few millivolts. It is a modification of the retro-active D. C. Voltmeter described in the April 1938 issue of the Wireless Engineer, and dispenses with the coupling battery.

The circuit is shown in Fig. (1). Both the valves are 6V6G, R_1 is 30,000 Ohms and r is 75 Ohms. The screen voltage of the 1st

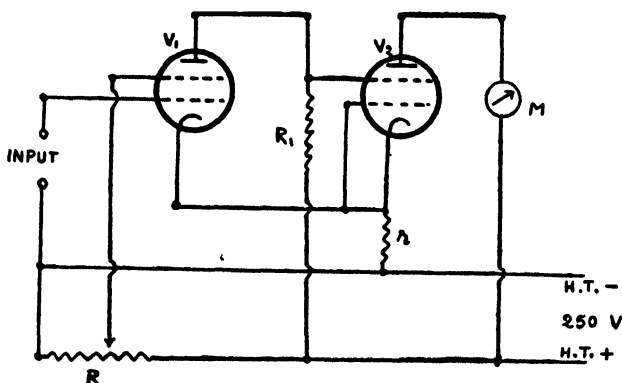


Fig. 1

valve and the plate voltage are respectively 45 and 250 volts. (The screen voltage however has to be adjusted for every individual valve according to the condition of the valve). The characteristic curve of the circuit is shown in Fig. (2).

From the point of view of the modification proposed, the ordinary pentodes have not proved to be as useful as the so-called

beam-valves ; but some other valves are also being tried with a view to get not only higher mutual conductance but also an improved shape of the characteristic curve of the circuit.

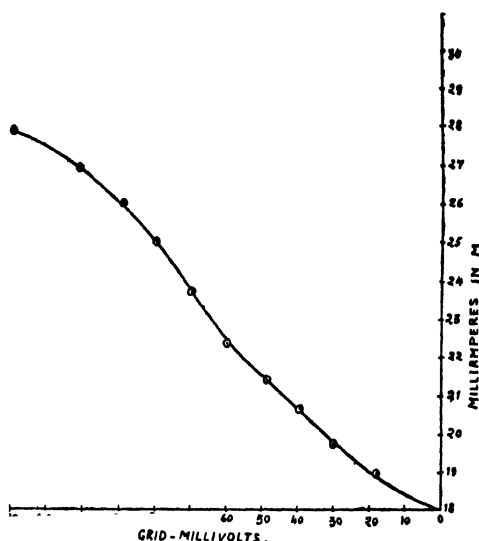


Fig. 2

There is one more advantage in choosing a suitable working point over the characteristic by changing the screen voltage of the 1st valve instead of applying an external bias voltage to its control grid.

The main point of interest, however, is the compact and self-contained nature of the instrument.

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NOTES AND NEWS

The 1940 Madras Session of the Indian Science Congress Association will be unique in the history of the Congress in as much as there is a proposal to open a new section called the section of

"Science and its Social Relations" during this session.

This new section will in time to come perhaps become the most important of all the present existing sections, as they will derive their inspiration from it and to some extent be guided by it in the direction of their researches. Similar sections have already been added to the American and British Associations for the Advancement of Science. The newly opened Section will appoint a Committee whose task will be "to consider",

with special reference to India and Indian conditions, "the progress, interconnections and new directions of advance in the mechanical, physical, chemical and biological sciences, especially in order to survey, at suitable intervals, and to promote thought upon the development of the scientific world picture, and upon the social significance of the applications of science".

When the Committees on Science and its Social Relations (C. S. S. R.) sitting in different countries will issue their reports and when these reports are collected, classified and reproduced after careful consideration by the International Council of Scientific Unions (I.C.S.U.) (under whose inspiration the Committees are working) in the form of a collective Report it will be a most useful document. This will no doubt enable us

to solve, to some extent, some of our problems, provide for some more amenities of life and help us to a little better understanding of our relations with one another.

The motto of science thus far has been truth and pure research and increase of knowledge for its own sake, and the scientists thought that their task was fulfilled when they finished their investigations of relationships in their own particular domain and left others to decide about the uses that can be made of their researches and to judge of the values of these uses. Thanks to the deliberations of the

British and American Associations for the Advancement of Science at their annual meetings as a result of the misuse or abuse of science for destructive purposes and the consequent starting of the International Council of Scientific Unions and of the different Committees on "Science and its Social Relations" and the well-thought-out questionnaire issued by them, that the view point is now changed. Science now considers loyalty not only to Truth but also to Justice as the guiding factors for the evolution of humanity towards a higher goal. Scientists do not now consider their task to be fulfilled by carrying on mere research, however classical it may be, but take a broader view of their social responsibility and consider their work in relation to the problems presented by human society. They also bear in mind the problems of the investigation of the social effects of science and the ethical problems involved in these effects. It is a matter of congratulation that the outlook of the scientist is now widened and the idea of his social responsibility broadened which will no doubt lead to a greater growth of human understanding and cooperation.

We have nothing but admiration for the excellent programme of work as outlined by the C.S.S.R. in Europe. The stress laid on the need for synthesizing thought and the study of relations between science and society and of the ever growing complexities of the relations among men is indeed praiseworthy. We would like to point out, however, that while the study of man's relations with one another is important, the study of man himself as to what he really is, what is his purpose in life, what is his goal is still more important, and how far the results of the investigations of the C.S.S.R. will be fruitful will depend entirely upon what conception is held as regards the constitution of man himself. We are of the opinion that unless and until man is recognized as a spiritual being the conception of man will ever remain incomplete; the diagnosis of his troubles only partial and hence the problems of poverty, unemployment and war with which humanity is faced and the problem of misuse of Science by unscrupulous countries in times of war with the consequent threat to civilization, will not be completely solved. If we scientists think that man is only body and mind and that there is nothing beyond mind like intuition (Buddhi) and will (Spirit, Atma), then in my humble opinion we shall not be able to take a synthetic view of the present situation and of the many

complicated problems confronting humanity. This view needs to be stressed.

* * * *

Western scientific civilization is receiving some hard knocks at the present day. The conditions obtaining in the world now show that might is right. The reason is not far to seek. The Western civilization is carrying its own seeds of destruction because it is based on materialism. The present conflict in the world and the consequent threat to civilization are the result of fundamental maladjustments and lack of perception of the essential values of life. To put forward this view before the scientists assembled in the next session of the Science Congress to be held in Madras and through it to give a definite lead to the scientific thought of the world the following Resolution has been sent to the Hon. General Secretary. India is a land of Sages and Seers who were pioneers in the Science of Life. She is therefore just the country which could wisely guide the thought of the world in the proper channels at this critical juncture.

RESOLUTION

The 1940 Madras Session of the Indian Science Congress Association is of the opinion that the present conflict in the world and the dire threat to civilization which it implies are due to fundamental maladjustments and lack of perception of the true values of life.

Having regard to the fact that the present war has been declared to be a war for the vindication of the principles of justice, freedom and international brotherhood, the Congress proclaims that in order to bring about proper adjustment in society between the advance of science and social progress, the spiritual and moral values must come first, the intellectual values next, and finally, though by no means to be overlooked or minimized, the values of material satisfaction.

The Congress is of the opinion that the solution of the economic problem, poverty, unemployment, etc. lies in such a readjustment and in the recognition and affirmation of the supremacy of spiritual and moral values.

The Congress further is of the opinion that this right environment and culture brought about as a result of the right adjustment will lead to the use of science for beneficent and humanitarian purposes and not for exploitation or destruction.

The Congress finally resolves to open a new Section of the Congress to be called the Section of "Science and its Social Relations" to indicate the importance it attaches to the development of social science.

D. D. K.

NATIONAL PLANNING

The present European War has served to bring home to us in no uncertain manner our economic dependence. The textile industry, one of the biggest industries in the country, is hard hit due to the difficulty of obtaining the necessary supplies of dyes and bleaching materials most of which have to be imported. The prices of many necessities of life including medicinal requirements have risen fabulously. The heavy chemical industry in the country has suffered considerably due to the difficulty of getting supplies from abroad of essential raw materials like sulphur and sodium nitrate. It is gratifying to learn that industrialists in the country, in co-operation with the Government, have started deliberations with the view of starting various new industries, although it must be admitted, a number of difficulties in the way of getting the required raw materials and particularly plant and machinery will have to be faced.

This brings us to the work of the National Planning Committee which was appointed by the conference of Ministers of Industries, which was held in Delhi in October 1938. This conference was of the opinion that :—

Problems of poverty and unemployment, of National Defence, and of the economic regeneration of India cannot be solved without industrialisation. As a step towards such industrialisation, a comprehensive scheme of National Planning should be formulated. The scheme should provide for the development of heavy key industries, medium scale industries and cottage industries, keeping in view our national requirements, the resources of the country, and the peculiar circumstances present in the country. Pending the submission and consideration of a comprehensive industrial plan for the whole of India, steps should be taken to start the following large scale industries of national importance on an all India basis :—

- (a) Manufacture of machinery and plant and tools of all kinds ;

- (b) Manufacture of automobiles, motor boats etc. and their accessories ;
- (c) Manufacture of electrical plant and accessories ;
- (d) Manufacture of heavy chemicals and fertilisers ;
- (e) Metal production ;
- (f) Industries connected with power generation and power supply.

With a view to carrying out the necessary preliminary work, the conference appointed a National Planning Committee, with Pandit Jawaharlal Nehru as Chairman and Prof. K. T. Shah, as Honorary General Secretary.

In this country, this is the first attempt to plan on a national basis, and to coordinate the manifold activities of the nation. The scope of the work of the committee has been kept very wide, and embraces all phases of national life having a bearing on the welfare of the people. The main objective which has been laid down for planning is to ensure an adequate standard of living for the masses, which means an increase in the national wealth. For purposes of planning, an increase of national wealth from two to three times during the course of the next ten years has been adopted as the minimum to be aimed at.

In order to have fullest assistance and cooperation of others in this gigantic task, the Planning Committee has appointed a number of sub-committees consisting of eminent and distinguished experts in various fields. The sub-committees appointed include those for cottage and rural industries, power and fuel, chemicals, mining and metallurgical industries, engineering industries, public utility industries and technical education. The final report of the Planning Committee will be awaited with great interest by the country.

R. C. S.

Book Reviews

An Introduction to the Calculus: By K. R. Gunjkar, M.A. (Cantab), B.Sc., I.E.S. (Oxford University Press), pp. 341. Rs. 4. Bombay, 1938.

The book is the result of the author's long experience as a teacher at the Elphinstone College and the Royal Institute of Science, Bombay. The author's aim in this book appears to make it possible for an ordinary reader with an elementary knowledge of Algebra and Trigonometry, to follow the subject of Calculus without any guidance. The clear and precise explanation on Limits and Continuity on which rests the whole superstructure of Calculus, the treatment given to Differentials, the theory of Real Numbers, Logarithmic and Exponential Functions which are generally passed over in other introductory books on the subject, would certainly create and stimulate in the readers a liking for the subject.

The author's love for writing in details together with the close print and the small types used at many places in the book are likely, at times, to exhaust the patience of a beginner and mar an otherwise good quality of the book.

S. M. SHAH.

Text-Book of Heat: By R. W. Stewart and John Satterly. Second Edition. Revised by C. T. Archer, published by the University Tutorial Press, Ltd., London, 1939. Price 7s. 6d.

This is a comprehensive treatise on heat meant for University students of both the Intermediate and Subsidiary B.Sc. standards. It has been revised by Mr. C. T. Archer, from the old and original work of Stewart and Satterly. The book treats almost all portions on classical heat in an elementary manner, so that it will rightly suit those students for whom it is meant. It is, however, doubtful whether the book will serve its utility as a text-book to those University students who have to study besides physics, a variety of other subjects for their examination. In junior classes, where the fundamentals of the different branches of physics are to be studied, the detailed knowledge of any one of

its branches, such as heat could not, with due justice, be assimilated. As a supplement to other general text-books on physics, this publication is of immense value. The special feature that one comes across and which can be commended to readers is the richness of matter pertaining to experimental side of the subject. In every section, all possible-types of laboratory and other experiments have been included, a feature which has enhanced the value of the book considerably. Specimen examples have been solved wherever necessary, to illustrate the application of theory to specific problems. A good number of intelligent exercises and examination questions with their answers has been appended at the end, in order to make the book appeal in general to University students.

One does not understand, however, how the author who claims to have modernised the portions in this book, remains satisfied by mentioning that the lowest temperature reached so far was -272.3°C. , while in fact, actually a temperature of 0.005° above abs. zero has been reached at Leyden as far back as 1935. This is not a point which should go against the intrinsic merit of the book as one of the classical works on heat.

N. R. T.

Practical Chemistry: By N. M. Shah. Fourth Edition. The Students' Own Book Depot, Dharwar. 1938. pp. 96+69 with appendices. Price Rs. 2 annas 4.

Nine years can be considered a short period for the appearance of the fourth edition of a book like Dr. N. M. Shah's "Practical Chemistry" for F.Y.Sc., and Inter. Science Courses. It bears ample testimony to the usefulness of the book which has proved a valuable guide to the students of these classes. The present edition which has been brought out with some improvements and additions, completely meets the requirements of the new F.Y.Sc. and Inter. Science Curriculum under the new bifurcation scheme.

The book has been mainly divided into two parts. The first part deals with quantitative analysis, gravimetric and volumetric, and the preparation and properties of gases. The systematic qualitative analysis of simple salts forms the subject matter of the second part. The last 9 pages of the book deal with a scheme for the identification of Simple Organic Compounds.

Special attention has been paid to emphasise the fundamental principles of theoretical chemistry on which the practical work is based, and to show how experimental results and calculations should be neatly and systematically entered in Journals. Neat simple diagrams add to the usefulness of the publication.

The book can be safely recommended for the students for whom it is intended.

R. C. S.

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- Chief Librarian, Library of the R. Swedish Academy of Sciences, Stockholm 50, Sweden.
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Department of Agriculture and Commerce, Scientific Library Division, Manilla, Phillipine Islands.

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Director General of Archæology in India, New Delhi.

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NOTICE

According to the revised scheme of the University Journal, Volume VIII is now complete with this Biological Sciences issue, part 5. Title page and Index will be sent in due course.

STRUCTURE AND BIONOMICS OF *ONCIDIUM VERRACULATUM*, CUV*

By

P. R. AWATI, B.A. (Cantab.), I.E.S.

AND

K. R. KARANDIKAR, B.A., M.Sc., Ph.D.

Zoology Department, Royal Institute of Science, Bombay.

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(A) SYSTEMATIC POSITION

Oncidium verraculatum, a marine slug, belongs to the family Oncidiidae of the class Gastropoda in the phylum

The work included in this paper was first carried out, in its general outline, by the junior author, during 1925-1927, under the directions of the senior author, and submitted in the form of a thesis to the Bombay University for his M.Sc. Degree. After a lapse of some years the senior author worked out in detail the circulatory system of this slug and published the same in the *Journal of the Bombay University* in 1933. After another lapse the junior author has had a fresh opportunity during 1938-39 to revise his previous studies and supplement them by fresh dissections, interpretations and diagrams. The present paper is thus the outcome of a piece of work which was first undertaken some fourteen years back, but which, for one reason or other, could not be brought to the stage of completion and publication till now.

Mollusca. The details of its classification are as follows:—Gastropoda is divided into two sub-classes:—(I) *Streptoneura*, (II) *Euthyneura*.

I. *Streptoneura*:—Sexes separate. Visceral loop twisted in the figure 8. Pallial complex placed anteriorly. Mostly a single ctenidium situated in front of the heart. Foot with an operculum for closing the shell.

II. *Euthyneura*:—Sexes combined (hermaphrodite). Visceral loop untwisted. Ctenidium when present lies posterior to the heart. Radula generally composed of rows of uniform teeth on each side of the median row. Head generally with two pairs of tentacles. Cerebral nervous system aggregated in the cephalic region.

Euthyneura is divided into two orders:—(1) *Opisthobranchia*, (2) *Pulmonata*.

(1) *Opisthobranchia*:—Marine forms with aquatic respiration. Pallial cavity when present is widely open. Ventricle of heart generally anterior in position. Tendency to reduction of shell which may occupy an internal position or disappear altogether (*Aplysia*, *Doris*, *Triton*, *Bulla*, *Eolis*, etc.).

(2) *Pulmonata*:—Pallial cavity present but no ctenidium. Pallial aperture is diminished by fusion of the mantle border with the neck, and reduced to a comparatively small, contractile orifice at its posterior extremity. Shell often reduced. Shell partially covered with integument, or internal, or even absent. No operculum in adult stage, although it may be present in post-embryonic stage particularly of marine forms. In the pallial cavity the inner wall of the mantle is traversed by vascular arborization, and thus constitutes the pulmonary organ for breathing air. Auricle usually anterior. Kidney with an ureter. Ganglia of the nervous system concentrated round the oesophagus and lying in close apposition to one another. No free larval stage. If a veliger is developed, it is always contained within the egg-membrane.

Pulmonata is divided into two sub-orders:—(i) *Basommatophora*, and (ii) *Stylommatophora*.

(i) *Basommatophora*:—External shell present. Head with a single pair of contractile but not invaginable tentacles bearing eyes. Penis situated at some distance from the female aperture. Veliger larva present.

(ii) *Stylommatophora* :—Generally two pairs of tentacles, contractile and invaginable. Eyes borne on posterior pair. No veliger larva except in *Oncidium*.

Stylommatophora is divided into two families:—(A) *Veronicellidae*, and (B) *Oncidiidae*.

(A) *Veronicellidae* :—Terrestrial, naked, limaciform, and shell-less. Anus posterior. Female genital aperture situated on the right side in the middle of the body. (Vaginula).

(B) *Oncidiidae* :—Marine, naked, limaciform, and shell-less. Female genital aperture at the posterior end of the body near anus. A reduced pulmonary cavity with a distinct pneumostoma.

Oncidiidae contains six genera—(a) *Peronia*, (b) *Oncidina*, (c) *Oncidiella*, (d) *Wastoniella*, (e) *Oncis*, (f) *Oncidium*.

The distinguishing characteristics of these genera, according to Hoffman are :—

(a) *Peronia*.—Male opening on the outer side of right tentacle. No hyponotal line. Eyes present.

(b) *Oncidina*.—Male opening on the outer side of right tentacle. No hyponotal line. Eyes absent.

(c) *Oncidiella*.—Male opening on the outer side of right tentacle. Hyponotal line present.

(d) *Wastoniella*.—Male opening on the inner side of right tentacle. No hyponotal line. Notal gland present. Hyponotum with many gland pores. Body-cavity divided by septum.

(e) *Oncis*.—Male opening on the inner side of right tentacle. No hyponotal line. Hyponotum broad or broader than foot. Rectal gland present. Penial gland absent. Lung and nephridium half symmetrical. Body-cavity undivided.

(f) *Oncidium*.—Male opening on the inner side of right tentacle. No hyponotal line. Hyponotum narrower than foot. Rectal gland absent. Penial gland present or absent. Lung and nephridium symmetrical. Body-cavity single, no septum.

Indian species of *Oncidium* are (i) *O. peronia*, (ii) *O. simrothi*, and (iii) *O. verraculatum*.

(B) EXTERNAL MORPHOLOGY

Oncidium verraculatum (Fig. 1) is a small marine slug, somewhat elliptical in outline, convex on its upper surface, flat on the lower side, and slate-grey in colour. The dorsal surface of the slug is formed by the *mantle* which is thickly covered with *tubercles* (tb). The latter show a wide variety in form, size and structure, ranging from minute granules to large protu-

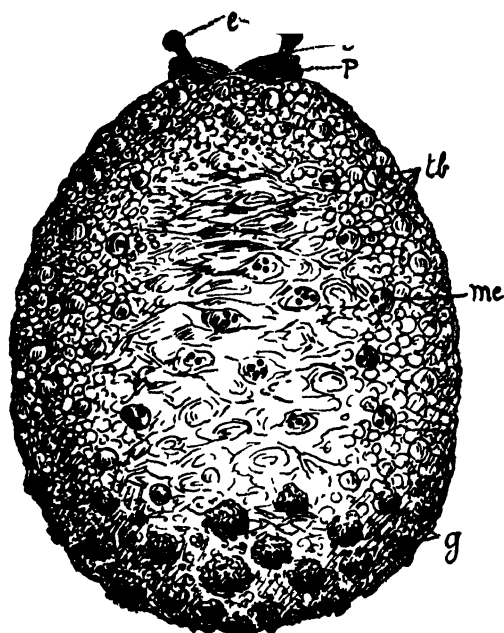


Fig. 1. A *dorsal* view of *O. verraculatum*.

e—Tentacular eyes. g—Gill-trees or branched tubercles. me—Dorsal tubercle bearing eyes. P—Labial palp. t—Tentacle. tb—Dorsal tubercles.

berances, scattered all over the dorsal surface. Some of the tubercles, especially those situated in the posterior region of the mantle, are irregularly branched and have in general a bushy appearance, by reason of which they are commonly known as "gill-trees" (g). Many others of the unbranched type have their free ends flattened, on which are situated a type of visual organs called the dorsal or *mantle eyes* (me). On account of the presence of these eyes these tubercles are known as *ocular papillae*. The mantle eyes may be located singly or in groups, the latter generally consisting of two or more on each ocular tubercle. The largest ocular group has been observed to contain six eye-spots, but 3—4-eyed groups are of common occurrence. The maximum number of eyes counted in a single specimen reached 54.

The ventral surface of the body is occupied by a medially situated, elongate, fleshy pad called the *foot* (Fig. 2. f). The latter is surrounded on all sides by the peripheral extension of the mantle, known commonly as the *hyponotum* (h). It is distinguishable, according to its location, into the *right*, the *left*, the

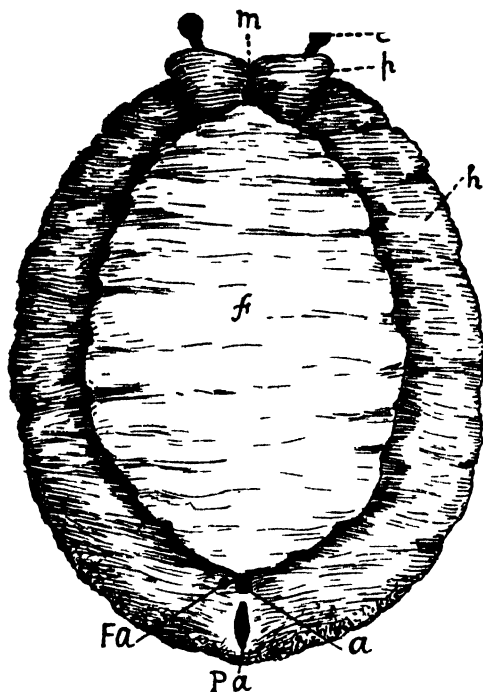


Fig. 2. A *ventral* view of *O. verraculatum*.

a—Anus. e—Tentacular eyes. f—Foot. Fa—Female genital aperture.
h—Hyponotum. p—Labial palp. Pa—Pulmonary aperture.

front, and the *hind* hyponotal regions. The relative measurements of the breadth of the foot and the right or left hyponotal region, have been used in classifying the different genera of these slugs.

The *mouth* (m) is situated at the anterior end of the body between the foot and the front hyponotum, and is bounded laterally by a pair of fleshy lobes called the *labial palps* (p) also known as oral lappets. In the antero-lateral corners of these palps is situated a pair of slender retractile *tentacles* (t) which carry the usual *cephalic eyes* (e) at their tips. Between the tentacle and the labial palp, on the right side, is located the male genital opening of this slug. Just behind the mouth, between it and the foot, is seen another small aperture which forms the exit of a large multicellular gland called the *pedal gland*. At the hind end of the body, on the ventral side are seen three apertures, situated between the foot and the hyponotum. Of these the one placed in the median line is the

anus (a). To the right of the anal opening lies the *female genital aperture* (Fa), while posterior to the anus is located a large *slit* (Pa) which leads inside into the *pulmonary* chamber of this slug.

Between the hyponotum and the foot on both the sides are seen a pair of longitudinal grooves which extend along the whole length of the animal, and which are completely hidden from view by the outwardly sloping edges of the foot. The groove on the right side starts from the female genital aperture in the posterior region, and runs anteriorly towards the opening of the pedal gland, situated between the mouth and the foot-extremity. Plate (1893) suggests that this groove serves as a channel for conveying the spermatozoa from the penis to the vagina for the purpose of self-fertilisation, for which reason he names it as the "genital groove." But structurally this appears to be improbable, in view of the fact that the groove in question has

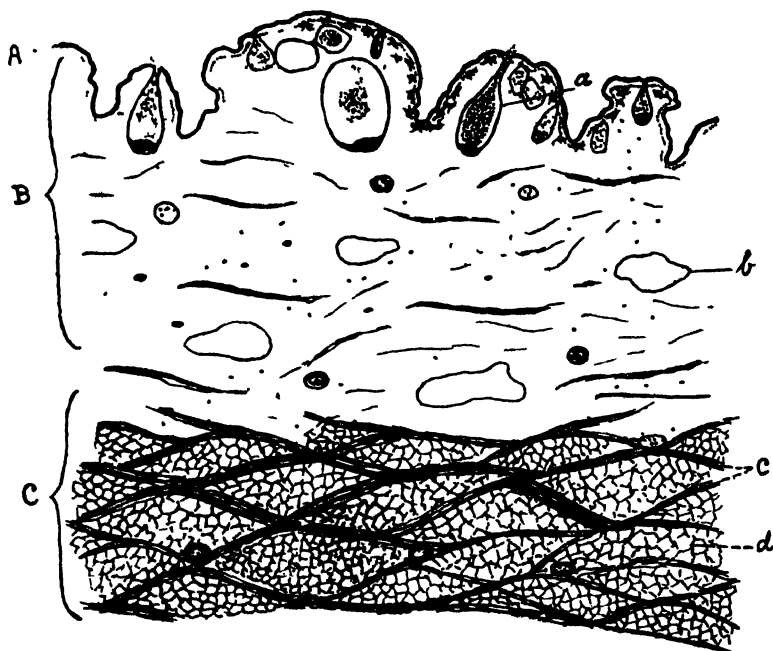


FIG. 3. Transverse section of the *mantle* or integument. $\times 40$.

A - Epidermis. B - Connective tissue. C - Muscle layer. a - unicellular gland. b - Blood lacunae c - Transverse muscle fibres. d - Longitudinal muscle fibres.

no connection at all with the anteriorly placed, male genital aperture. On the other hand it terminates in the vicinity of the opening of the pedal gland, as mentioned above. Our observations on *O. verraculatum* indicate that there is one longitudinal groove on *each* side of the foot instead of one on the right side only, as found by Watson (1926) in *Oncidiella*, and that these grooves very likely serve as suckers by producing a vacuum which enables the slug to anchor itself fast to the substratum.

(C) INTERNAL ANATOMY

(1) INTEGUMENTARY SYSTEM

The mantle which forms the dorsal covering for the enclosed body-organs, is relatively thin in the mid-dorsal region and thick at the sides. A transverse section of the mantle (Fig. 3) shows that it is formed of various tissues which, commencing from the outermost are the epidermis (A), the connective tissue (B), and the muscular layer (C). The epidermis is formed of a single layer of columnar epithelium (Fig. 4. b) with conspicuous

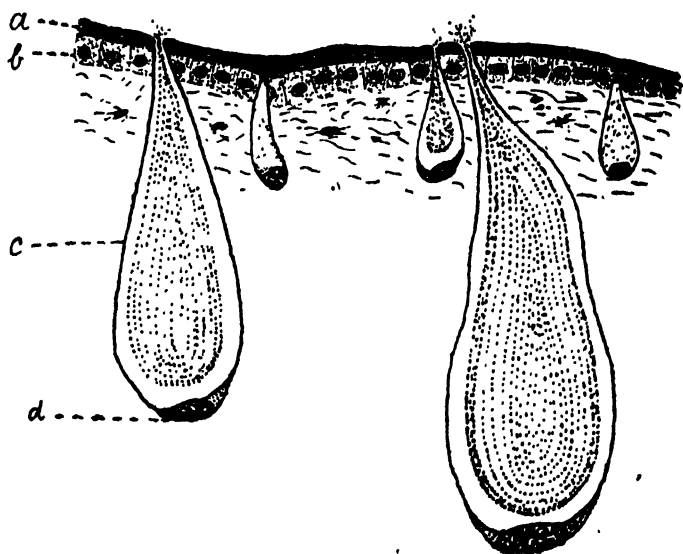


FIG. 4.

Transverse section of the *mantle* showing unicellular glands. $\times 400$.

a—Cuticular lining. b—Columnar layer. c—Unicellular gland. d—Nucleus. nuclei situated basally in the cells. Along the outer side of the columnar layer is a thin cuticular coating (a) secreted by the columnar epithelium. Below the epidermis

lies a thick mass formed of connective tissue cells and fibres (Fig. 3. B). In this tissue are seen a few muscle fibres, some irregular empty spaces called the blood-lacunae (b), and the transversely cut arterial branches and nerve fibres. One also sees a large number of sac-like glands (a), situated in this tissue-mass and opening to the outside through small necklike apertures. The innermost portion of the mantle-wall is formed by the muscular layer (Fig. 3. C.) consisting of *longitudinal* (d) and *transverse* (c) muscle bands running into each other in a network-like fashion. Of these three distinct tissues forming the mantle or body-wall, the connective tissue layer occupies a greater space than either of the other two.

The histology of the foot is slightly different from that of the mantle-wall described above. Here the connective tissue layer is rather thickly packed with transversely running muscle fibres. This has presumably a physiological significance in view of the locomotory function of the foot-organ.

Mucous glands.—In close association with the epidermal tissue is found a system of glands which is so characteristic a

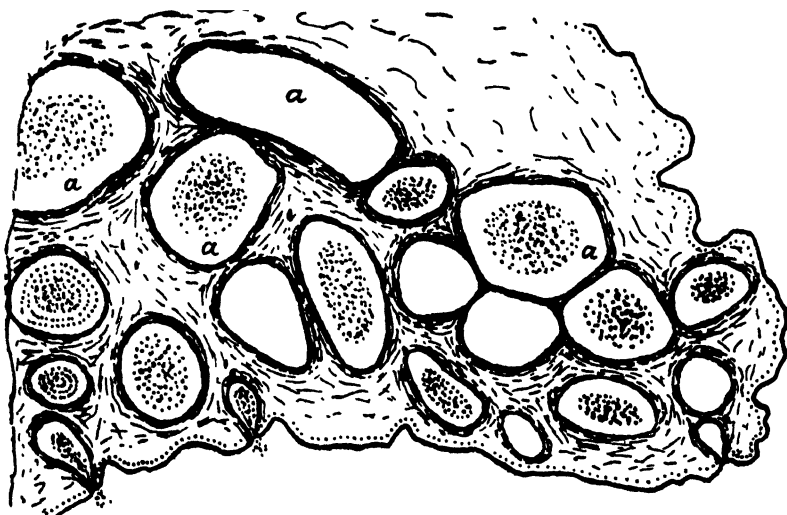


Fig. 5. Transverse section of the *hyponotal margin* showing the multicellular glands (a) $\times 60$.

feature of the family *Oncidiidae*. A casual examination of the hyponotal region of the slug under study, shows the presence

of innumerable, minute, pale-white specks scattered all over the surface. These represent the glands which secrete fluid mucus rendering the animal slimy to touch. The glands are of two types: Unicellular and multicellular. A *unicellular gland* (Fig. 4. c) is formed by a physiological modification from one of the columnar cells of the epidermal layer. As it starts to secrete the mucus fluid, it grows in size and attains the form of a large, elongate goblet-like sac filled with mucus secretion, the cell-nucleus (d) being more or less pushed down to the bottom of the cell-bag. At the slightest touch the animal can usually be observed to eject a large quantity of the fluid through the narrow neck of this glandular bag opening on the surface. Unicellular glands are situated in the surface layer of the body-integument, though they are specially abundant in the foot, particularly, along its peripheral region.

A *multicellular gland* is formed by an invagination of the epithelial layer, resulting in the formation of a large central cavity bounded by a wall of secretory cells. Such glands are abundantly found in the right and left hyponotal regions of this slug. (Fig. 5. a).

In addition to the integumentary, mucus-secreting glands, there is one more special gland situated in the anterior portion of the foot. By reason of its location in the foot-region, it is known as the *pedal gland*, which extends at one end into the body-cavity, just below the central nervous system, and opens at the other to the outside a little behind the mouth, and becomes continuous with the longitudinal groove as mentioned above.

(2) DIGESTIVE SYSTEM

The *mouth* (Fig. 2. m) opens on the ventral surface of the head region between the foot and the head-hyponotum, and is bounded laterally by a pair of labial lobes (p). It leads within into the buccal cavity (Fig. 7. a) along an oblique passage which is slightly eversible and which has its walls thrown into conspicuous longitudinal folds. The buccal region is continued behind into a large swollen, bulb-like, muscular pharynx (b). The posterior portion of the pharyngeal bulb shows a pair of prominent swellings (c), between which stands a median knob-like projection called the *radula papilla* (Plate, 1892). The walls of the pharynx are thrown into conspicuous folds (Fig. 8), and within the cavity is situated a rasping organ, the *radula* (d).

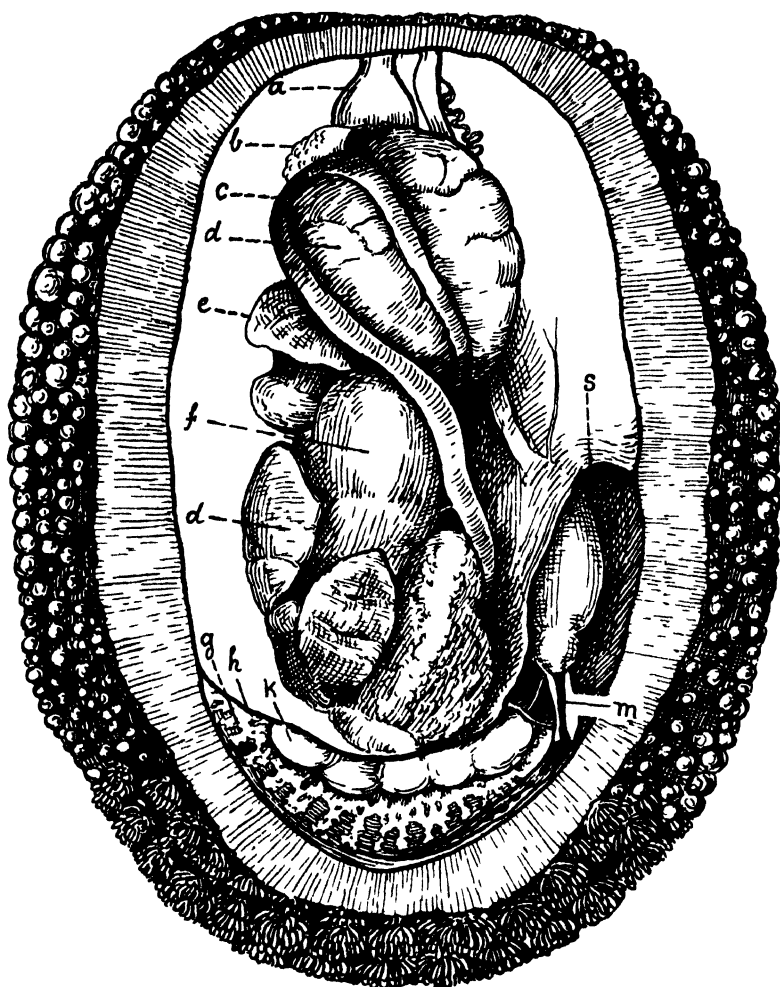


FIG. 6. A *dissected* specimen of *O. verraculatum* showing the internal organs *in situ*.

a—Pharyngeal bulb. b—Salivary gland. c—Intestinal loop. d—Liver lobe. e—Stomach. f—Gizzard. g—Pulmonary chamber. h—Diaphragm. k—Nephridium m—Tendinous cord. s—Septum separating pericardium from body-cavity.

The radula when dissected and stretched out appears somewhat rectangular in form, and has its anterior margin broadly conical (Fig. 9). It is beset with transverse rows of teeth arranged on either side of a single, median, longitudinal row. In its

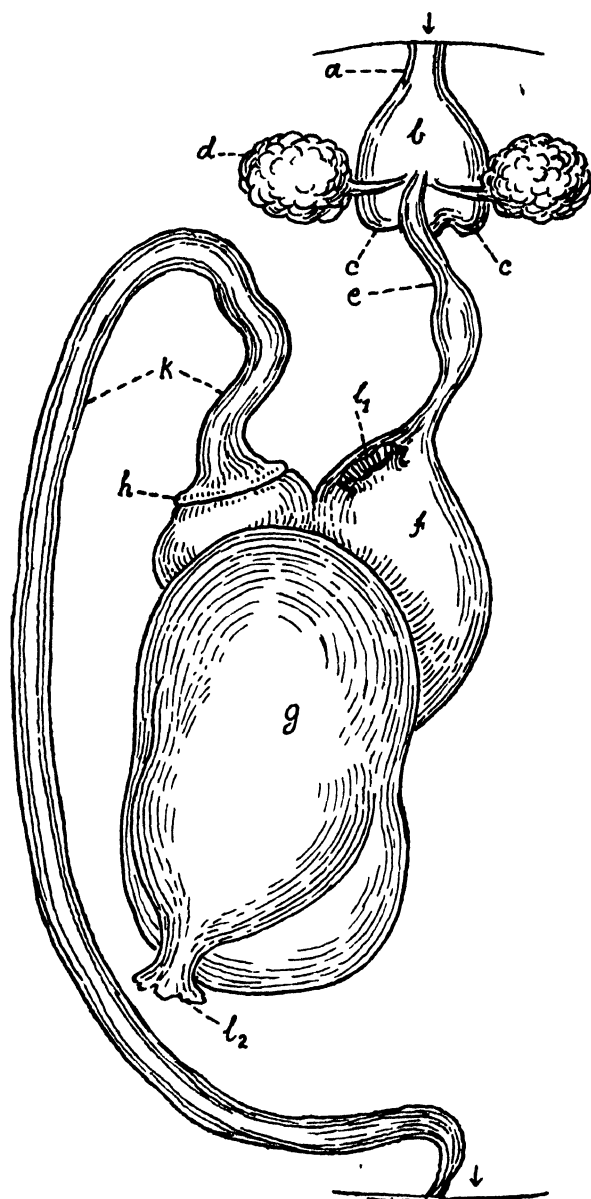


FIG. 7. *Alimentary canal of O. verraculatum.*

a—Buccal region. b—Pharyngeal bulb. c—Lateral swellings of pharyngeal bulb. d—Salivary gland. e—Oesophagus. f—Crop. g—Gizzard. h—Stomach. k—Intestine. l_1 l_2 ,—Liver openings.

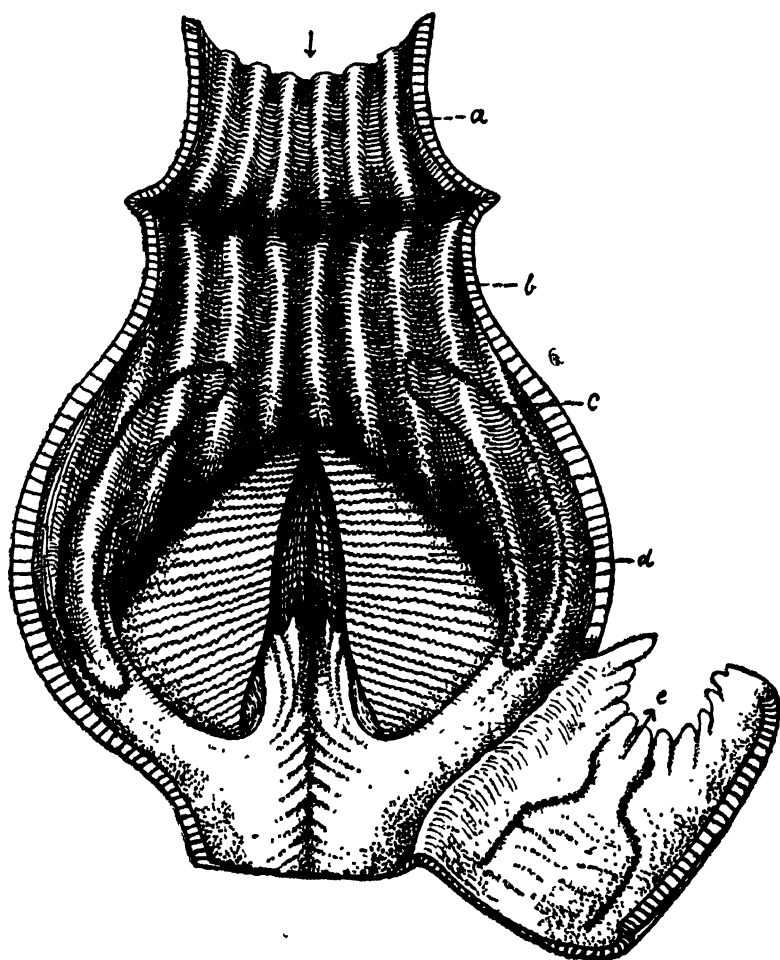


FIG. 8. Horizontal section through the *buccal* and *pharyngeal* regions showing the folds on the wall and the centrally situated *radula*.

a—Buccal region. b—Pharyngeal region. c—Teeth row on pharyngeal wall. d—Radula. e—Passage leading to oesophagus

natural position the posterior portion of the radula is rolled into a tube (Fig. 10), with the dentate surface forming its inner wall. The anterior portion of the radular plate is folded on itself, so that the dentate surface in this region lies facing the pharyngeal wall (Fig. 11). It is this anterior portion of the radula with its broadly conical border, that remains exposed in the pharyngeal cavity, and that operates in the rasping function

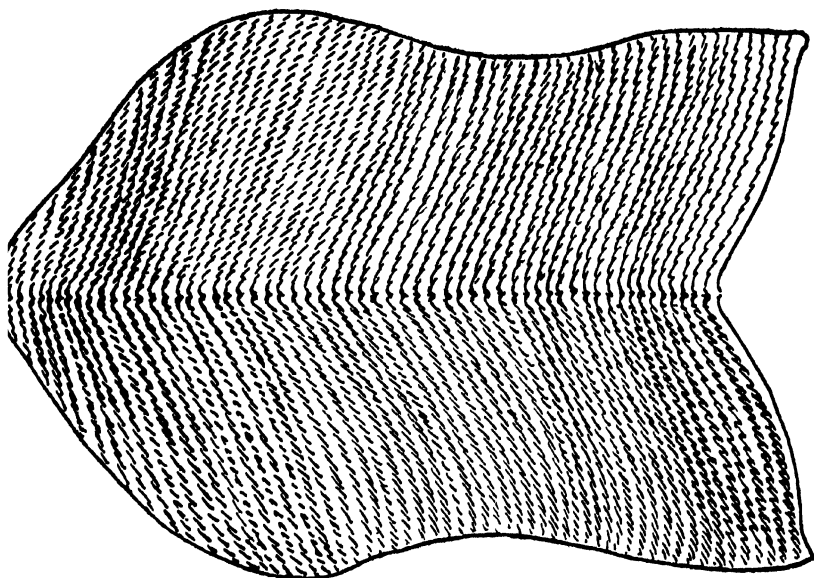


FIG. 9. *Radula* dissected and stretched out. $\times 18$.

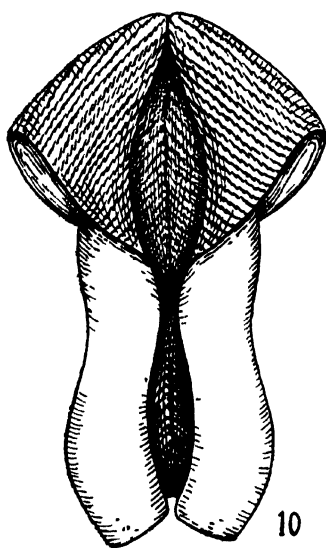


FIG. 10.
Radula, dorsal view. $\times 18$.

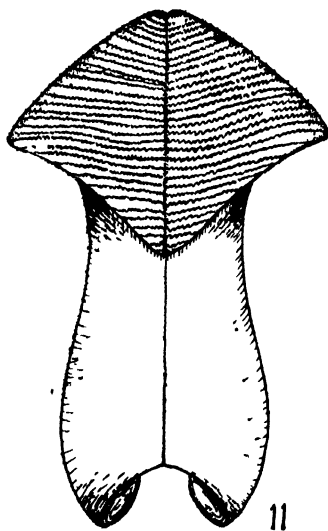


FIG. 11.
Radula, ventral view. $\times 18$.

when the food is taken in. The radular tube is filled with an elastic tissue formed of fibres and cells, scattered and embedded in a homogeneous, non-cellular, ground-substance (Fig. 14. g). The posterior end of the radular tube is inserted into what is known as the *radular sac* which on the outer surface of the pharynx constitutes the *radula-papilla* mentioned above (Fig. 18. n). The margins of the folded anterior portion of the radula are joined to the wall of the pharynx by means of a thin membrane which is capable of great flexion, and which thus allows the backward and forward movement of the radular apparatus. The radula is supported on a pair of thick elastic spoon-like plates which together constitute the "radula-support" (Figs. 12. 13. 14. e). The two spoon-like plates are joined to each other along their median ventral line by means of a semi-

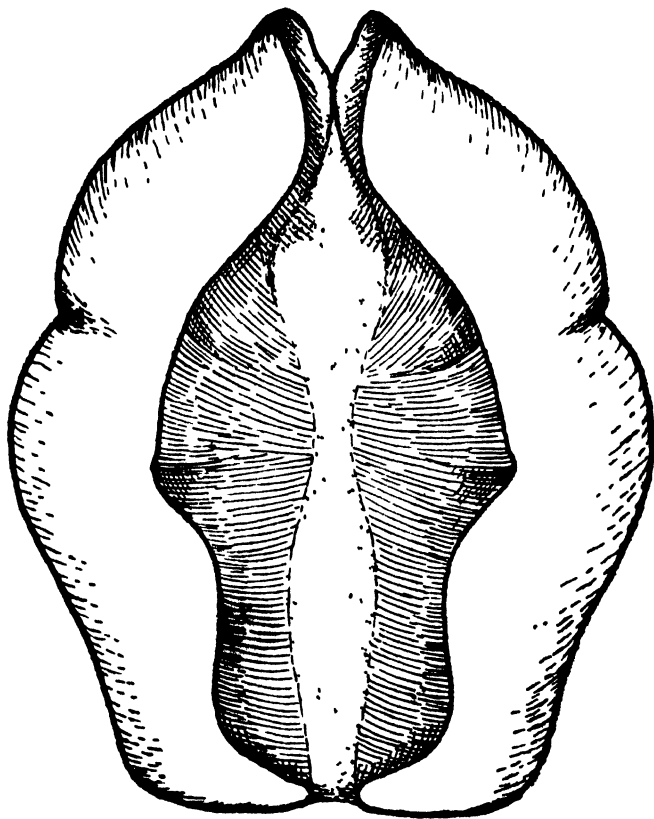


FIG. 12. *Radula-support*. $\times 15$.

transparent, elastic tissue, and thus take on the form of cushion-like *pads* supporting the radula on its ventro-lateral sides. The posterior corners of the radula-support are heavily clothed with muscle bands, by reason of which are developed the two prominent *lateral swellings* (Fig. 7. c) of the pharyngeal bulb mentioned above.

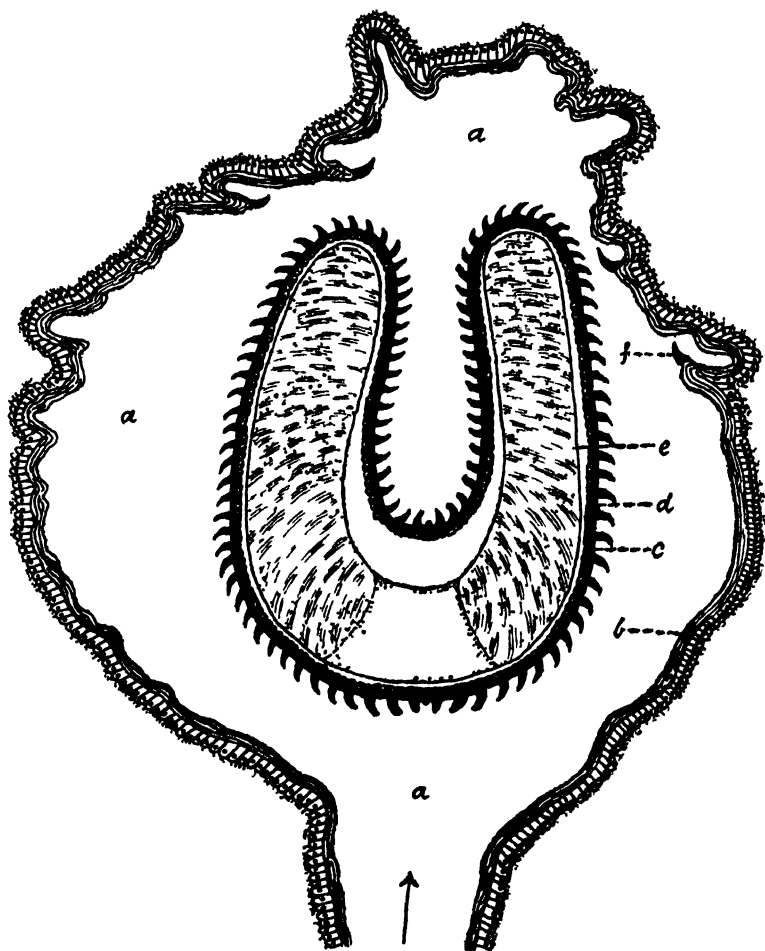


FIG. 13. Transverse section through the anterior region of *pharynx*, showing the radula-apparatus cut across. $\times 70$.

a—Pharyngeal cavity. b—Chitinous lining of pharyngeal wall formed of columnar cells. c—Radula bearing teeth d—Odontoblast cells which secrete the radular stuff. e—Radula support or cushion. f—Pharyngeal teeth.

Figure 13 gives a transverse section passing through the anterior region of the pharynx. The pharyngeal wall is seen lined with a chitinous coating, showing the two pairs of palatal teeth (*f*) situated dorso-laterally. Within the pharyngeal cavity is seen the radular apparatus cut transversely, and lying free and disconnected from the pharyngeal wall. The section also shows the radular ribbon involuted in the mid-dorsal line. Just below the ribbon is situated a layer of cells called odontoblasts (*d*) which secrete the radular stuff (Joyeux Laffaie, 1882). The central core of the radular apparatus is occupied by the "radula support" in the form of the cushion-like pads (*e*).

Figure 14 is another transverse section passing through the middle region of the pharyngeal bulb. The pharyngeal cavity is seen here confined only to the dorsal side of the radula apparatus. The radula has the form of a closed tube with in-turned margins, and teeth projecting inwards. The core of the radular tube is occupied by the elastic non-cellular substance

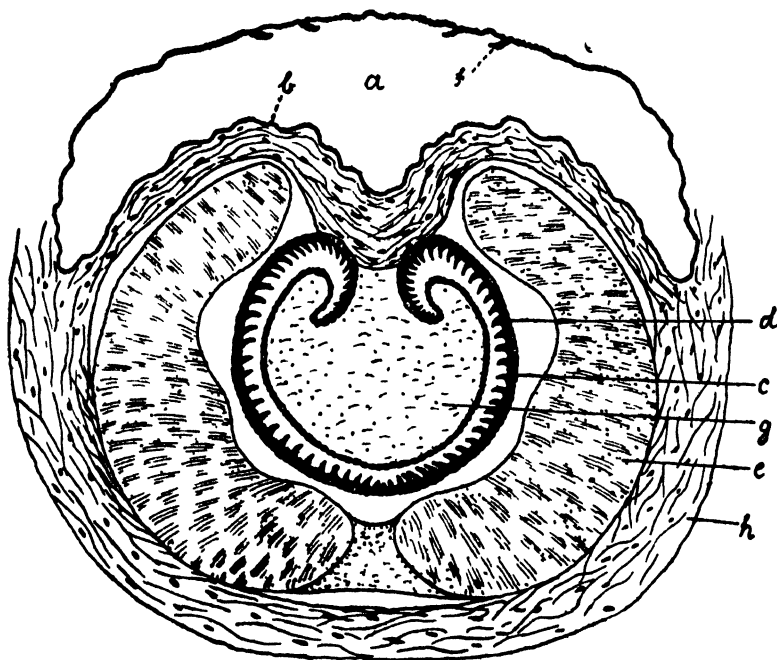


FIG. 14. Transverse section through the posterior region of the *pharynx* showing the radular tube cut across. $\times 60$.

g—Non-cellular elastic tissue occupying the lumen of radular tube.
h—Muscular coat surrounding radula apparatus. Other lettering as in Fig. 13.

(g) described above. The "radula-support" (e) which apparently occupies a central position in Fig. 13, is situated here outside to the radula-tube, and is thickly wrapped with a strong muscular clothing.

The *histology* of the "radula-support" is rather complex. Joyeux Laffuie (1882) states that the radula support is composed of cartilagenous matter which is similar to the fibro-cartilage of Vertebrates. Plate (1892) who expresses his doubts regarding the view of the French writer, does not however go any further in elucidating the point. He simply describes the structure of this organ, without assigning any histological homology for the same. In the course of our investigation, microtome sections of the radula-support have shown it to contain muscle-fibres spreading through a cellular body formed of transparent, polygonal cells with small nuclei (Fig. 15). When treated with 5% potash solution, the radula-support was found to soften and dissolve completely.

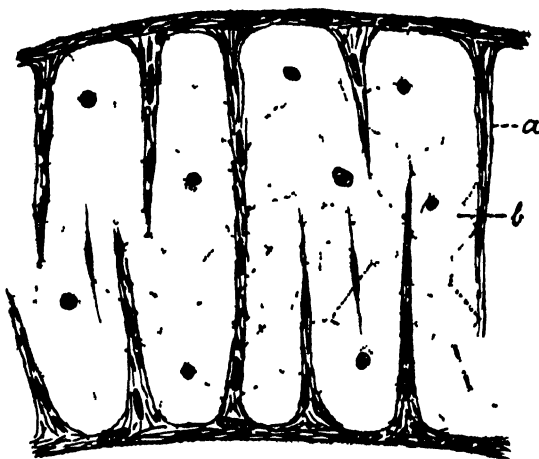


FIG. 15. Section through the *radula-cushion*. $\times 320$.

a — Muscle bands. b — Polygonal cells.

The *radula* as already mentioned, is a chitinous plate bearing teeth on its surface. The teeth are arranged symmetrically in transverse rows which spread out at an angle on either side of the median row and then run straight towards the margins. The anterior border of the radula is broadly conical, with the result that the number of teeth in each transverse row gradually increases as one starts to count them from the anteriormost point. The first transverse row, for instance, carried only six teeth on

each side, while the next one following contained ten. The maximum number of teeth in a single row on each side of the median row of the same specimen, reached seventy-three. It must be mentioned here that the numbers of teeth and rows vary between different individuals, as may be seen from the table given below. These variations are presumably due to the factor of age of the specimens concerned.

Table giving the length and breadth of the body, and the numbers of teeth and rows in the radula of O. verraculatum

Specimen	Length of body	Breadth of body	Rows of Teeth	Teeth-formula
1	6.5cm.	4cm.	65	66-1-66
2	5.8cm.	3.7cm.	60	59-1-59
3	6.2cm.	3.9cm.	64	62-1-62
4	6.4cm.	4.1cm.	68	68-1-68
5	6.6cm.	4.3cm.	68	69-1-69
6	6.9cm.	4.4cm.	70	73-1-73

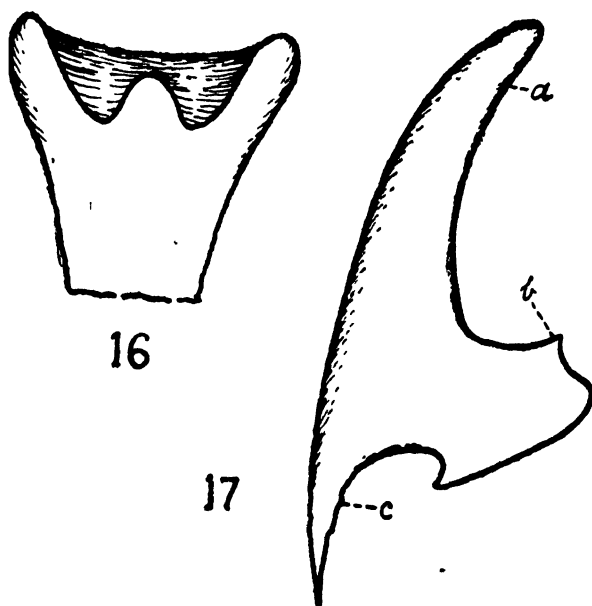


FIG. 16. "Central" tooth from the radula. $\times 600$.

FIG. 17. "Lateral" tooth from the radula. $\times 320$.

The radular teeth are of two kinds, in respect of their structure and form. The teeth from the median longitudinal row, known as "centrals", are *tricuspid* in form (Fig. 16), being provided with three symmetrically arranged cusps or cones directed anteriorly. The lateral cusps called *ectocones* are slightly longer and narrower than the central *mesocone*. The teeth from the transverse rows, known as "laterals", are asymmetrically *bicuspid* in form (Fig. 17). Each tooth possesses one long, curved, strongly developed, conical process (a) directed anteriorly, and a second small, blunt elevation (b) near its base. From the latter is given off proximally another process (c) by which the tooth is planted into the chitinous substance of the radular plate. Of the laterals, the three proximal teeth on each side, and a few others near the periphery, are generally not so strongly developed as the rest.

In addition to the radular apparatus described above, the pharyngeal wall of the slug also carries from four to six rows of small chitinous processes or teeth (palatal plates, Berge 1882) situated laterally, in a diagonal direction (Figs. 8. c; 13, 14. f).

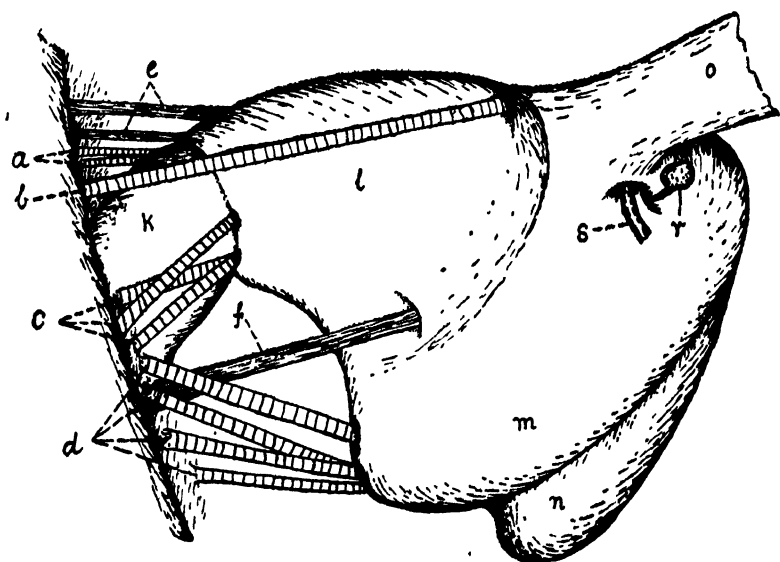


FIG. 18. *Pharyngeal bulb* showing the muscular system.

a—Dorsal anterior protractors. e—Ventral anterior protractors.
b—Dorsal posterior protractors. d—Ventral posterior protractors.
e—Dorsal retractors. f—Latero-ventral retractors. k—Buccal region.
l—Pharynx. m—Lateral swelling. n—Radular papilla (sac). o—Oesophagus.
r—Nerve ring. s—Salivary duct.

The principal *function* of the radula is to rasp off food-particles from the food-material taken in by the slug. In this function the radular apparatus has to perform a backward and forward movement within the pharyngeal cavity. This movement is effected by means of muscle-bands stretching between the pharyngeal bulb and the body-wall. These muscles fall into two categories, according to the functions they perform in the movement of the bulb and the contained radula. Some are called *protractors*, while the others go by the name *retractors*. There are four sets of protractors and two sets of retractors, distinguishable according to the locations wherein they are situated. In *Figure 18* (*a, b, c, d*) are the four sets of protractors known as *dorsal anterior, dorsal posterior, ventral anterior, and ventral posterior protractors* respectively. The same *Figure* shows also the two sets of retractors : *dorsal* (*e*) and *latero-ventral* (*f*) in position.

The *oesophagus* (*Fig. 7. e*) arises from the mid-dorsal region of the pharynx and turns postero-ventrally over the pharyngeal bulb. After passing through the nerve-ring it runs behind along the floor of the body-cavity and enters into a large, swollen region called stomach. A *transverse section* of the oesophagus (*Fig. 19*)

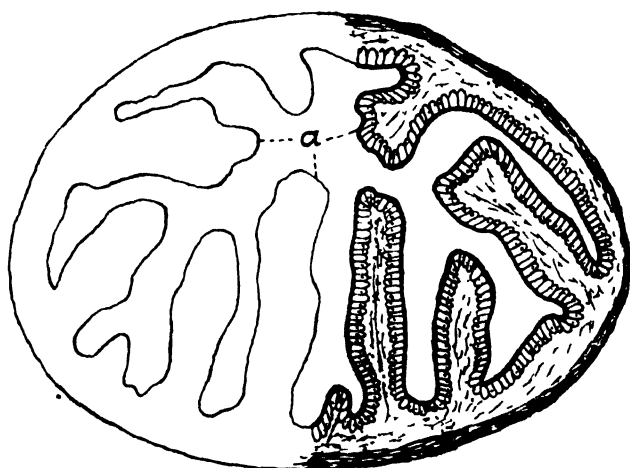


FIG. 19. Transverse section of the *oesophagus*. $\times 160$. a—Folds.

shows the inner wall thrown into conspicuous folds (*a*). The oesophageal wall is formed of three layers. The innermost layer is formed of columnar epithelium (*Fig. 20. b*) which secretes the

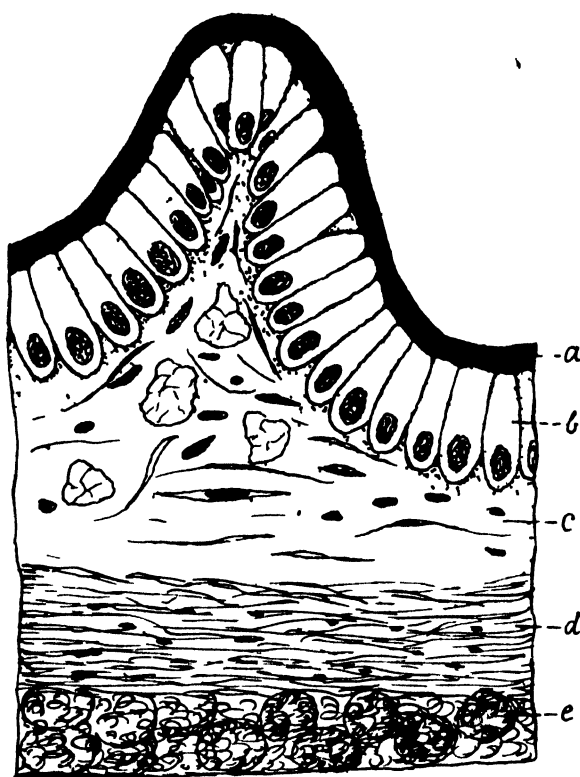


FIG. 20.

Section of an *oesophageal fold* highly magnified. $\times 1000$.

a - Cuticular lining. b - Columnar epithelium. c - Connective tissue.
d - Transverse muscles. e - Longitudinal muscles

inner chitinous lining (a). The middle layer (c) is formed of loose connective tissue containing blood-vessels, open spaces and nerve endings. The outermost is the muscular layer which is made up of an inner layer of circular (d) and an outer layer of longitudinal muscle-fibres.

A sagittal section through the *stomach* region (Fig. 21) shows it to be formed of three different chambers of which the antero-lateral one on the right side is the *crop* (b), the posterior one is the *gizzard* (c), and the antero-lateral one on the left side is the *stomach* proper (d). The *crop* is a thin-walled sac into which opens the liver-gland by a pair of ducts situated just below and above the oesophageal entrance respectively. The *gizzard* which constitutes the second chamber of the stomach region is a strongly

muscular and heavily swollen structure. The sagittal section shows its walls to be formed of strong muscle-bands which are

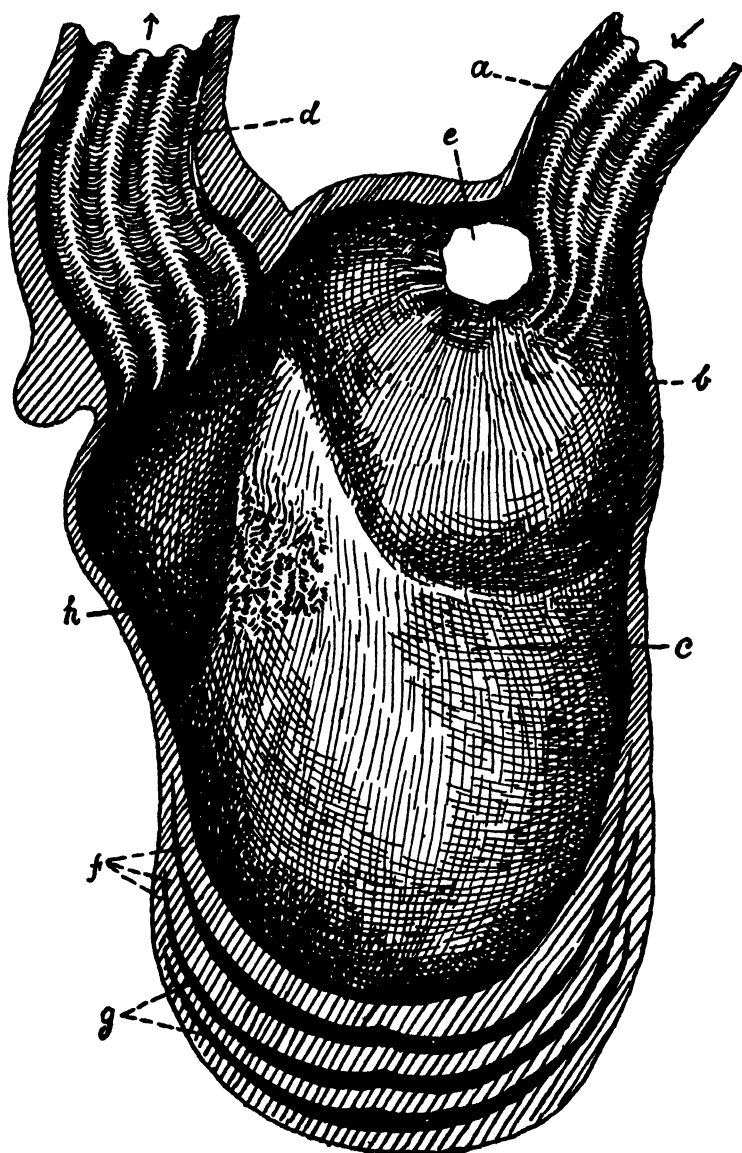


FIG. 21. Sagittal section through *stomach*.

a - Oesophagus. b - Crop. c - Gizzard. d - Stomach. e - Opening of liver gland.
f - Muscle layers or strata. g - Connective tissue mass. h - Chitinous ridges.

arranged in layers or strata (f) one over another, the space between them being occupied by connective tissue (g). Internally the gizzard has a thick chitinous lining which in the left anterior corner gives rise to chitinous ridges (h) bearing minute teeth.

The *stomach* proper (Fig. 21.d) is a thick-walled chamber which proximally is in free communication with the crop and the gizzard. Distally it leads into the *intestine* (Fig. 7. k), the latter having the form of a long coiled tube. The intestine runs anteriorly for a short distance, then turns to the right, crosses over the oesophagus, turns again posteriorly, makes a dorsal loop, then runs diagonally over the digestive gland, makes another loop in the horizontal plane, then takes a posterior course and continues into the *rectum* which opens to the outside ventrally through the anus (Fig. 2. a). The rectum is joined by a duct called the *ureter* which empties its contents into the rectal passage for discharge to the outside through the anus.

A transverse section of the *stomach* (Fig. 22) shows the dendritic branching of the internal villi. The wall of the stomach

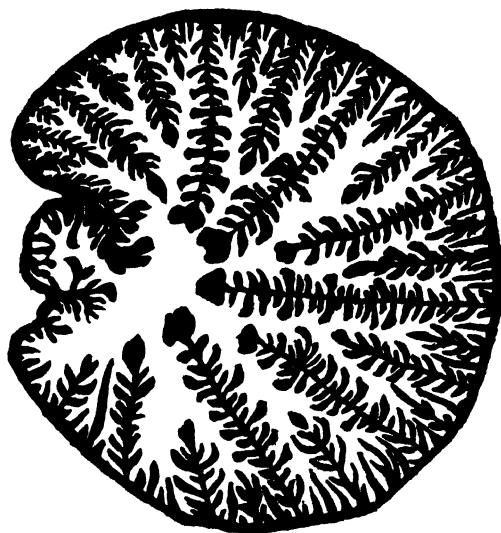


FIG. 22. Transverse section of *stomach* showing dendritic branching of villi. (Drawn from photograph).

is formed of the three typical tissue-layers of which the innermost is formed of ciliated columnar epithelium (Fig. 23. a). In-between the columnar cells are also seen a few goblet cells (b) of a secretory nature.

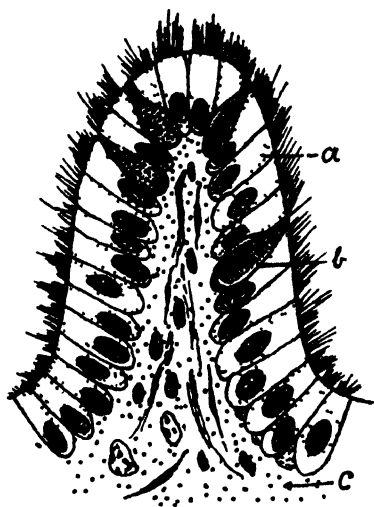


FIG. 23. A *stomach-villus* magnified. $\times 1000$.

a—Ciliated columnar epithelium.

b—Goblet cells.

c—Connective tissue.

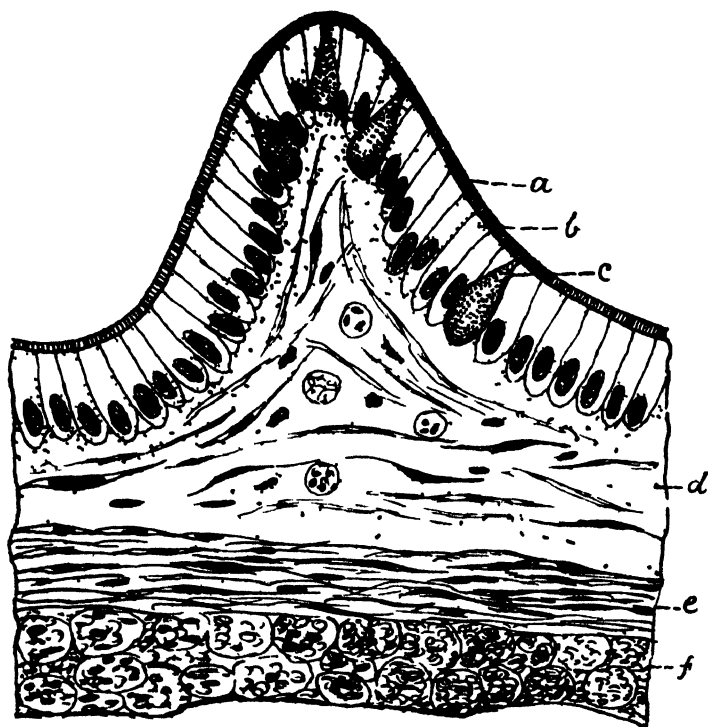


FIG. 24. Transverse section through an *intestinal villus*. $\times 1000$.

a—Striated border. b—Columnar epithelium. c—Goblet cells.

d—Connective tissue. e—Circular muscles. f—Longitudinal muscles.

A transverse section of the *intestine* shows its inner wall thrown into folds or villi. *Figure 24* shows one of the intestinal villi under high magnification. The histological structure of the intestinal villus is similar to that of the stomach except for the fact that the columnar epithelium of the intestinal wall is not ciliated as in the case of the stomach epithelium. The columnar layer shows, however, a thin cuticular coating on its free surface (a), which appears to be very much like the *striated border*, so characteristic of the digestive system of Insects and many lower Invertebrates.

Digestive glands.—These consist of a pair of *salivary glands* (Fig. 7. d) associated with the pharynx, and a three-lobed *liver mass* (Fig. 6. d) associated with the stomach region. The salivary gland has the appearance of a bunch of blunt finger-like processes (Fig. 25) connected with a central canal which opens into the pharyngeal cavity. The finger-like processes are formed of large and somewhat circular cells containing granular proto-

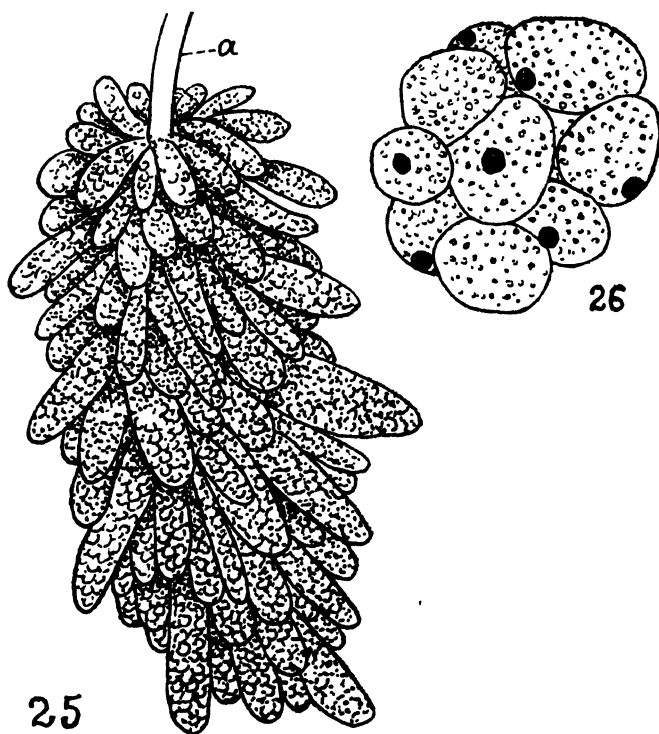


FIG. 25. *Salivary gland.* a—central duct.

FIG. 26. Section of *salivary gland* showing gland cells. $\times 480$.

plasm (Fig. 26). The salivary fluid secreted by these cells is emptied into small ductlets which open into the central duct which in turn pours the contents into the pharyngeal cavity, just near the base of the oesophagus.

The *liver mass* (Fig. 27) occupies a large space in the body-cavity. It is recognizable into three portions each opening separately either into the crop or into the gizzard. One portion of the liver mass located around the posterior region of the gizzard opens into the latter by a central duct (Fig. 7. l_2). The other two portions situated anteriorly and amongst which runs the intestinal tube making several loops, open by large separate ducts into the crop, below and above the entrance of the oesophagus (Figs. 7. l_1 . 21. e). The digestive gland (liver) is made up of lobules, each being composed of elongated secretory cells with round nuclei (Fig. 28). These hepatic cells pour their secretion into small ductlets which join with one another and give rise to a common hepatic duct pertaining to each liver lobe.

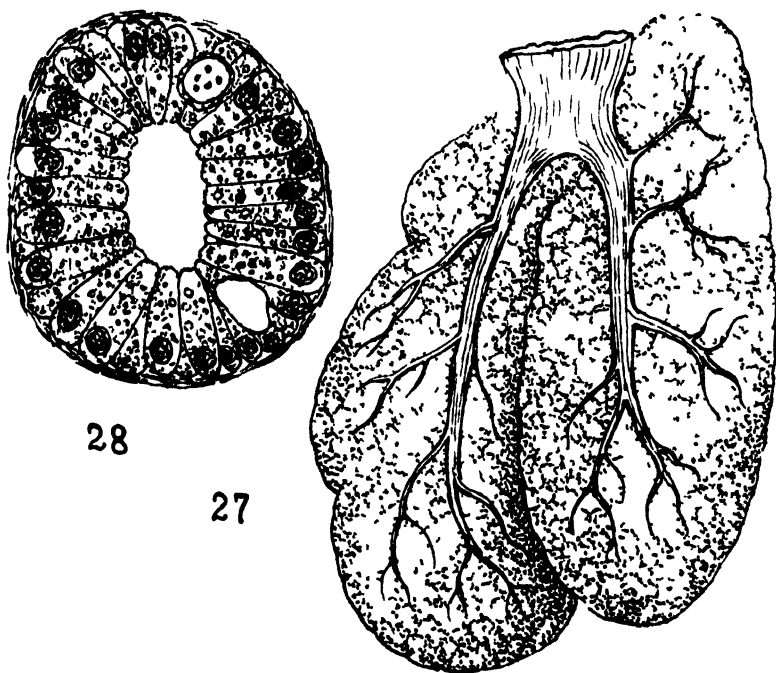


FIG. 27—*Liver lobes.* FIG. 28—*Section of a liver-lobule.* $\times 380$.

(3) RESPIRATORY SYSTEM

O. verraculatum is amphibious in its habitat and is, therefore, adapted to both the aquatic and the terrestrial types of respiration. The seat of aquatic respiration in this animal lies in its *mantle surface* or dorsal integument. The dorsal surface of the mantle is all beset with *tubercles* (Fig. 1. tb), varying in size and number. The tubercles have a surface layer of thin, elongated, columnar epithelium (Figs. 3, 4) through which oxygen is absorbed from the surrounding aquatic medium. It is an interesting sight to observe the slug spreading out its tubercles, when placed in water, so as to absorb as much oxygen dissolved in water as possible. Just beneath the layer of columnar epithelium is situated the connective tissue-mass containing a network of smaller blood-vessels and lacunæ. Blood is brought to these tubercles by branches of the paired *lateral* (mantle or longitudinal) *arteries* (Fig. 29, 30. a ; 33, 3). After gaseous exchange which takes place at the tuberculate surface, under aquatic conditions, the aerated blood is returned through blood-lacunæ which join each other and pour their contents into a pair of large *lateral sinuses* (Figs. 29, 30. b) at the sides, and an unpaired *median sinus* (Fig. 29. c) on the dorsal side. These sinuses convey the purified blood in due course to the heart through the pneumo-nephridial region described further on (Fig. 33).

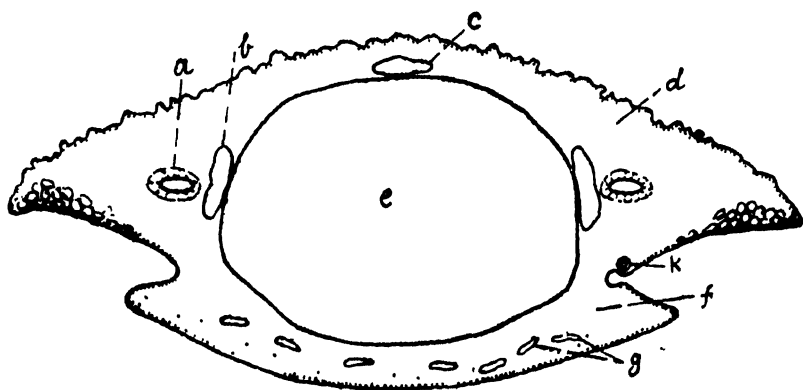


FIG. 29.

Transverse section of *Oncidium* showing *sinuses* and *arteries*. $\times 8$.

a—Mantle or lateral or longitudinal artery. b—Lateral sinus. c—Dorsal sinus. d—Mantle. e—Body-cavity. f—Foot. g—Pedal sinuses. k—Vas deferens.

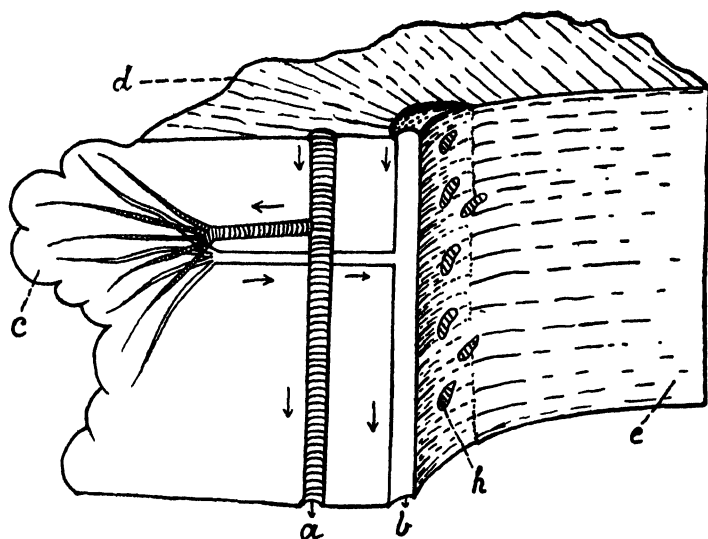


FIG. 30. Diagrammatic representation of the *circulation of blood* in the region of the mantle tubercles.

a — Mantle artery. b — Lateral sinus. c — Dorsal tubercle. d — Mantle.
e — Body-cavity wall. h — Pores opening into lateral sinus.

In addition to the mantle-surface serving for the aquatic mode of respiration, structural provision is also made for gaseous exchange between the blood and the atmospheric oxygen surrounding the animal, particularly under the terrestrial conditions of life. This provision consists in the presence of a special lung-like or *pulmonary cavity* (Fig. 31. c ; 33. g), situated in the posterior region of the body. It is a large chamber separated from the body-cavity by means of a muscular septum called the diaphragm (Fig. 33. e), and communicating with the outside through a small aperture (Fig. 2. Pa) opening on the ventral side in the vicinity of the anus. The inner wall of this chamber is thrown into a network of small irregular projections, obviously with the purpose of increasing the respiratory surface. These irregular processes are lined with a layer of very small and thickly packed epithelium having very minute nuclei (Fig. 32), the cell-membranes being very thin and almost indistinct even under the high power of the microscope. A network of blood-vessels and lacunæ is spread just beneath this epithelial lining. Atmospheric oxygen, taken into the pulmonary chamber through the pulmonary opening, passes into the sub-epithelial system of blood-circulation. After gaseous exchange the ærated blood is returned into the *dorsal* and *ventral pulmonary vessels*

(Fig. 33. 11, 14), and thence into the heart for its further circulation.

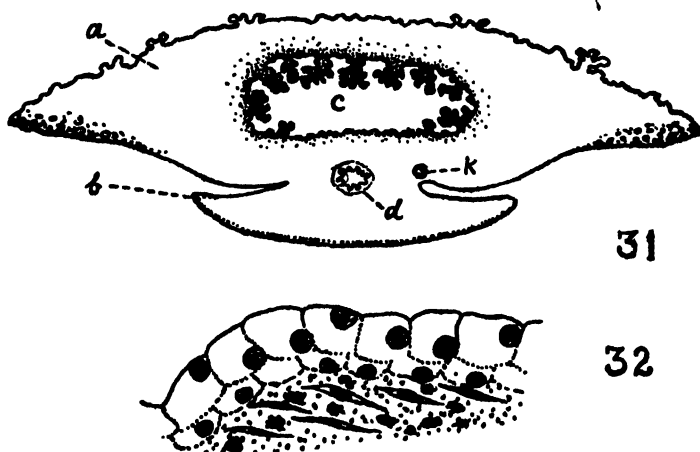


FIG. 31. Transverse section through *pulmonary* chamber $\times 8$.
a—Mantle. b—Foot. c—Pulmonary cavity. d—Rectum.

FIG. 32. Section through *pulmonary tissue* magnified. $\times 1250$.

That the pulmonary chamber is essentially meant for aerial respiration, can easily be seen from the fact that the pulmonary aperture is usually closed so long as the slug remains in water ; but even then if it wishes to take in air (which it does quite frequently under normal conditions), it simply lifts up the posterior region of its body, and thus raises up the aperture in question above the water-level, and then takes in air from the atmosphere. Moreover under submerged condition bubbles of gas are usually observed issuing from the pulmonary chamber through the aperture, indicating thereby that the chamber is definitely used for the aerial respiration.

(4) CIRCULATORY SYSTEM.

The circulatory system of *O. verraculatum* (Fig. 33) consists of the following parts:—(i) the heart, (ii) the arterial system, and (iii) the venous system.

Heart:—The heart consists of two chambers of which the anterior one is the *ventricle* (b) and the posterior one, the *auricle* (a). Both of them are enclosed in a somewhat elliptical cavity called the *pericardium* (c) which is situated on the right side of the animal, at about one-third the distance of its length

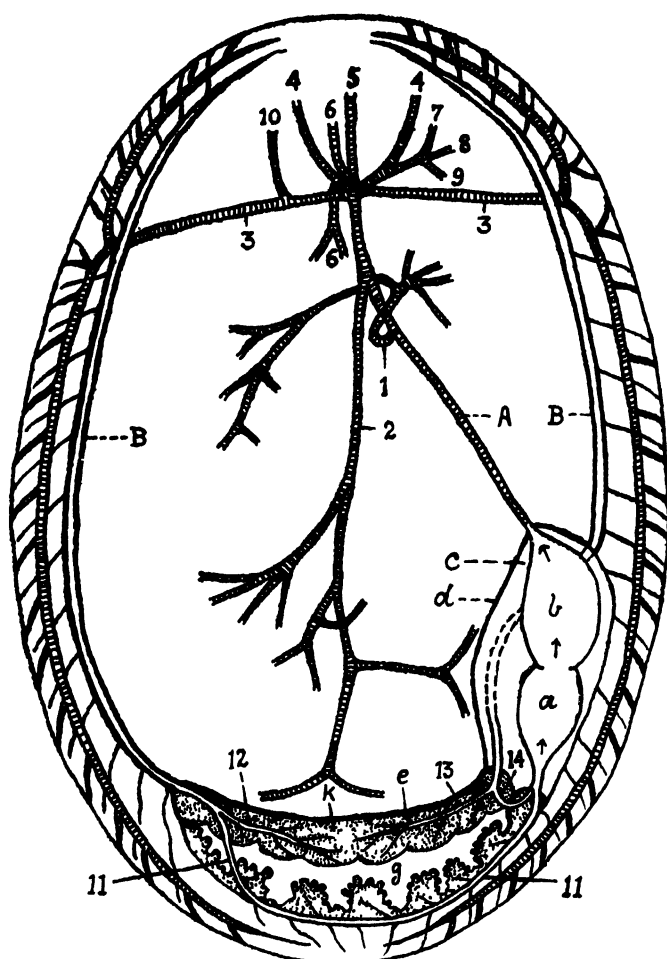


FIG. 33. *Circulatory system of O. verruculatum* (Diagrammatic).

a—Auricle. b—Ventricle. c—Pericardium. d—Pericardial septum. e—Diaphragm. g—Pulmonary chamber. k—Nephridium. A—Aorta. B—Lateral sinuses. 1—Visceral Artery. 2—Genital A. 3—Mantle or lateral or longitudinal A. 4—Tentacular A. 5—Pharyngeal A. 6—Pedal A. 7—Right salivary A. 8—Penial A. 9—Vas deferens A. 10—Left salivary A. 11—Dorsal pulmonary vessel. 12—Left smaller vessel to nephridium. 13—Right smaller vessel to nephridium. 14—Ventral pulmonary vessel.

from the posterior end. It is separated from the body-cavity by a thick *septum* (d) formed of connective tissue, and is lined from inside by a layer of pavement epithelium with flattened

cells and prominent nuclei. The pericardium does not communicate with the body-cavity, since the latter is a hæmocœle. The former however opens into the *nephridium* (k) through a ciliated reno-pericardial canal (Plate 1891), and thence indirectly to the outside through the ureter, rectum and anus. The pericardium thus forms a true coelomic cavity.

The *auricle* (a) is a thin-walled sac-like structure placed at the posterior end of the thick-walled and strongly muscular ventricle (b). At the extreme posterior end of the auricle two *pulmonary vessels* (11, 14) open into it, and at this junction it appears that the auricle originates as an onward continuation of

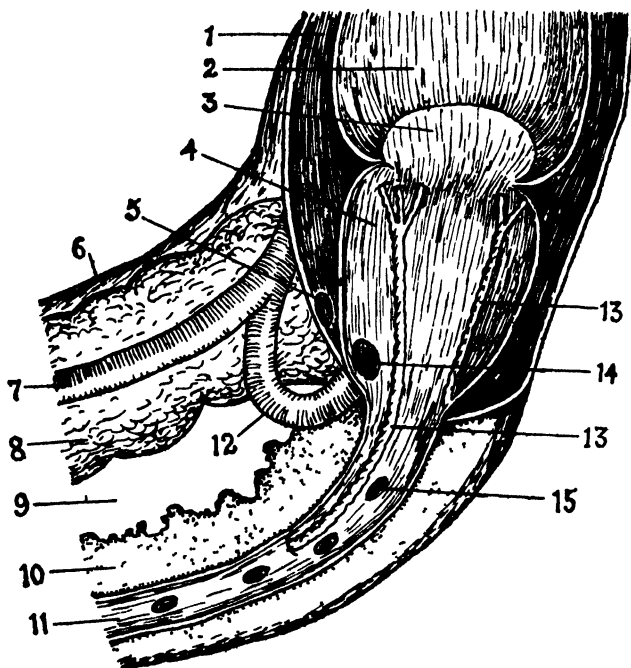


FIG. 34. A horizontal section through the *auricle* and the dorsal pulmonary vessel showing the attachment of "tendinous cords." (Diagrammatic).

1—Pericardium. 2—Ventricle. 3—Auriculo-ventricular valve. 4—Auricle. 5—Opening of Reno-pericardial canal. 6—Diaphragm. 7—Renal branch of right lateral sinus. 8—Nephridium. 9—Pulmonary cavity. 10—Pulmonary tissue. 11—Dorsal pulmonary vessel. 12—Ventral pulmonary vessel. 13—Tendinous cords. 14—Opening of (12) into the auricle. 15—Openings of smaller pulmonary sinuses into (11).

these vessels, particularly the *larger dorsal one* (11). The auricle when fully extended, assumes the shape of a large flask, with its short narrow neck being continuous with the pulmonary vessels, with sides bulging out, and the bottom flat and opening into the ventricle. The auricular cavity is traversed by numerous muscle-strands which arise by divisions among themselves from the original muscular layer passing round the inside of the auricular wall. Many of these muscle strands extend towards the anterior end of the auricle and get inserted into the base of the ventricle. Likewise two rather prominent muscle-bands stretch posteriorly towards the mouth of the dorsal pulmonary vessel, of which one gets attached to the posterior border of the opening, and the other extends within the passage and is fixed to the inner wall of the vessel in question (Fig. 34). These muscle-strands named by Cuvier as "tendinous cords," show longitudinal striations, when viewed under high magnification. The nuclei in them are somewhat spindle-shaped, the spindles lying parallel to the striations mentioned above (Awati, 1933).

At its anterior end the auricular wall is fused with that of the ventricle except in the middle portion where the two chambers communicate with each other. From this auriculo-ventricular junction project forward into the ventricular cavity two lengthwise, fleshy *flaps* (Fig. 35. b), formed of white fibrous tissue with scattered muscle fibres, and functioning as *valves*.



FIG. 35. Longitudinal section through heart and aorta $\times 16$.
a - Auricle. b - Auriculo-ventricular valve. c - Ventricle. d - Ventriculo-aortic valve. e - Vacuolated tissue surrounding aortic base.

As compared with the auricle, the *ventricle* (Fig. 35. c) is a thickly set muscular organ. Its inside is filled with muscle-bands, leaving thus a smaller lumen in the middle. It is somewhat pear-like in shape, the proximal end being broader than the distal one, the latter becoming continuous with the aortic trunk.

The *aorta*, at the point of its origin, contains a *valvular structure* (Fig. 35. d) which is membranous and attached at one end to the aortic base. It hangs freely into the aortic cavity and functions as a valve preventing the return of blood from the aorta to the ventricle.

Mechanism of the heart.—The auricle is pulled towards the dorsal pulmonary vessel by the contraction of the two "tendinous cords" attached to the inside of the vessel as mentioned above. Closely in the wake of this contraction the auricle gets filled with blood brought from the pulmonary vessels, followed by the blocking of the apertures of the latter. The auricular blood then forces its way through the auriculo-ventricular valves into the ventricle, partly under its own pressure and partly by the muscular action of the auricular wall. The ventricle in its turn contracts and drives its contents into the aorta, the aortic valve preventing the return of blood into the ventricle.

Arterial system (Fig. 33).—At the very outset an important structure needs to be mentioned here, which is characteristic of Oncidiidæ in general, and which supplies an easy guide to differentiate an arterial vessel from a venous one (including sinuses). Every artery in *Oncidium* is surrounded by a peculiar kind of tissue which in the living condition has a silvery appearance. In histological preparations the tissue in question appears to be formed of thin-walled cells with large vacuoles (Fig. 36. b). The latter seem to occupy nearly the

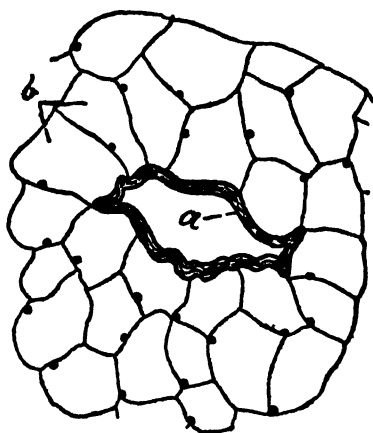


FIG. 36. Transverse section through an *artery*. $\times 300$.

a—Muscle ring surrounding the lumen of the artery. b—Large-celled vacuolated tissue surrounding the artery.

whole of the cell-spaces, the cell-nuclei, very small in size, being almost crowded out towards the periphery. Each artery in its transverse section (Fig. 36) shows two kinds of rings forming its wall, the inner one being a thin circle of muscle-fibres (a) lining the lumen, and the outer one being constituted by the vacuolated, silvery tissue (b) mentioned above. The presence of this characteristic structure helps to easily distinguish an artery from a vein or sinus in the animal under study.

The arterial system of *O. verraculatum* consists of a single *aorta* (Fig. 33. A) which issues from the anterior end of the ventricle and from which several arteries are given off to different body-organs and body-wall. The aorta is a thick, large vessel which runs anteriorly towards the central nervous mass. On its way it gives off a couple of branches: the visceral artery and the genital artery. The *visceral artery* (1) supplies blood to the different lobes of the liver and also to the stomach and the intestinal loops passing through the liver-mass. The *genital artery* (2) which is very extensive in its branching and distribution, supplies blood to the reproductive and other organs lying in the posterior region of the body-cavity, including the pericardium, the heart, the nephridium and the mantle-chamber.

At the central nervous mass, just below the oesophageal tube, the aortic trunk divides into six principal arteries. Of these arteries, two (3) branch off laterally from the main trunk, one on each side, and run towards the opposite body-wall. On entering the latter just below the lateral sinus (B), each artery divides into two branches of which one goes towards the anterior end, and the other towards the posterior end. Both the branches supply blood to the dorsal tubercles and the mantle-wall on each side. By reason of their location and distribution, these two right and left vessels, issuing directly from the aortic trunk are known as the *lateral or mantle arteries* (3) (Awati, 1933).

Anatomically, these *mantle arteries* were taken to be veins by previous writers. Joyeux Laffuie (1882) has described them as "branchio-cardiac veins"; and Plate (1893) seems to hold the same view. Watson (1925), when describing the circulatory system of *Oncidiella*, names these vessels as "longitudinal veins." But the presence of the vacuolated silvery tissue surrounding them all along their course through the mantle-wall, easily indicates, as has been proved by the senior author (1933), that these two vessels are not veins at all, but constitute a pair of *lateral or mantle arteries* supplying blood to the mantle-wall and the dorsal tubercles.

Antero-lateral to the point of origin of the mantle arteries, arise a pair of vessels, the *tentacular arteries* (4), one on each side, which circulate blood to the tentacles, the palpi and the cephalic eyes. The *right tentacular* artery gives off a branch which divides into three sub-branches of which one goes to the right salivary gland (7), another to the penial gland (8), and the third to the vas-deferens (9). The left salivary gland is supplied with blood from a branch (10) given off from the left mantle artery.

Between the two tentacular arteries the aortic trunk continues forward in the form of a median unpaired vessel, the *pharyngeal artery* (5) which circulates blood to the pharyngeal bulb and the buccal region. There is one more arterial vessel, known as the *pedal artery* (6) which arises ventrally from the aortic region. It bifurcates into two branches which run anteriorly and posteriorly respectively and supply blood to the foot.

Venous system (Fig. 33).—The venous circulation of *O. verruculatum* has been described in detail by the senior author (1933) elsewhere, of which the salient points only are incorporated into this account.

The body-cavity of this slug, as in all other *Oncidiidæ*, is hæmocœlic in its origin, and forms the main reservoir into which the venous blood from the visceral and reproductive organs is collected. From there it flows, through a series of slant-wise apertures, into a pair of large lateral channels or sinuses (B) running longitudinally through the tissue of the mantle border, one on each side of the mantle-cavity. Besides that from the body-cavity, venous blood from two other sources also flows into these lateral sinuses, the sources being the ventral foot-region and the lateral mantle-wall. The *foot* consists of a spongy tissue which encloses many small sinuses. The latter run into each other and form a pair of common channels which pour their contents into the lateral sinuses, in the posterior region of the body. All along the course of each lateral sinus a series of smaller sinuses open into it. They bring blood from the tubercles and "gill-trees", situated on the dorsal and lateral surface of the mantle, and supplied previously with arterial blood from the lateral or mantle arteries (3). As already mentioned these tubercles act as accessory respiratory structures under aquatic conditions. So the blood brought from them through small sinuses and poured into the large lateral sinuses, though apparently venous is really aerated and therefore arterial in its true nature.

Each lateral sinus (B) containing mixed blood from three different sources, divides into two unequal branches, in the pneumo-nephridial region. Of these branches, the bigger one, (11) on the *left* side, enters the tissue of the pulmonary chamber, passing on its way through the intervening nephridial mass, and is continued into the dorsal *pulmonary vessel* or vein (11), situated on the dorsal side of the lung cavity, just beneath the mantle. On the *right* side, the course of the lateral sinus is bent inwards below the pericardium, and its bigger branch (14) is likewise continued into the *ventral pulmonary vein* (14). The *smaller* branches (12, 13) of both the lateral sinuses enter the nephridial tissue (k) and break up there into minute irregular sinuses forming a network round the nephridial tubules. After the waste-products from the blood are excreted by the nephridial cells, the blood is then returned through a series of inter-nephridial sinuses into the two pulmonary vessels (11, 14).

Pulmonary vessels.—There are two pulmonary vessels or veins of unequal lengths. The longer one (11) which is a continuation of the bigger branch of the left lateral sinus, runs along the postero-dorsal side of the pulmonary cavity and opens at the right end into the auricle, and is for that reason known as the *dorsal pulmonary vein*. The other vessel (14) which is shorter in length and is likewise a continuation of the bigger branch of the right lateral sinus, lies on the antero-ventral side of the pulmonary chamber, and is called for that reason as the *ventral pulmonary vessel* or vein. Both these pulmonary vessels open into the auricle near each other, one being over the other. Through the opening of the dorsal vessel pass inwards into it from the auricle, the two “tendinous cords”, already mentioned in connection with the mechanism of the heart.

The blood conveyed to the auricle through the pulmonary vessels or veins, comes from four different regions: (i) aerated blood from the pulmonary chamber, (ii) blood from the inter-nephridial sinuses after being relieved of the excretory products in the nephridium, (iii) blood from the dorsal sinus* which is partly aerated in the dorsal tubercles, and (iv) blood from the posterior sinuses coming from the posterior region of the mantle.

* In addition to the two lateral sinuses, one more sinus is situated (Fig. 29. c) which passes through the mid-dorsal region of the mantle all along its length. In the pneumo-nephridial region the dorsal sinus breaks into two branches which pour their contents into the two pulmonary vessels respectively.

(5) EXCRETORY SYSTEM

The excretory system of *O. verraculatum* consists of a large, brownish gland called the *nephridium* (Fig. 33. K) which is situated in the pulmonary chamber, lying somewhat crosswise along the inner side of the diaphragm. It is formed of excretory tubules each lined with a single layer of distinct, flat cells (Fig. 37) containing large, spherical nuclei. The nephridial

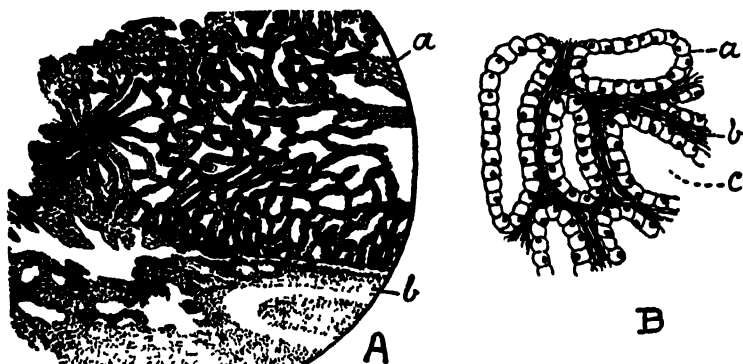


FIG. 37. A :—Section through *pneumo-nephridial* region. $\times 50$.
a—Nephridial tissue. b—Pulmonary wall.

B :—*Nephridial* tissue magnified. $\times 200$.

a—Nephridial tubule. b—Internephridial vessels or sinuses. c—Lumen of nephridial tubule lined by a single layer of flat cells.

tissue is traversed through by minute vessels of the smaller branch of each lateral sinus. The inter-nephridial vessels (B. b) surround the nephridial tubules (B. a) from which they may easily be distinguished by the absence of the epithelium of flat cells which line the tubules. Nitrogenous waste-products extracted from the internephridial blood are poured into a central wide canal called the *ureter* (Fig. 38) which leaves the nephridial gland on the left ventral side, runs a short distance posteriorly and then discharges its contents into the *rectum* and thence to the outside through the anus.

The venous blood from the internephridial vessels, after being deprived of its waste-products by the nephridial tubules, is led through a series of sinuses which pass for a short distance through the lung-tissue and ultimately open into the pulmonary veins, as described above in connection with the circulatory system.

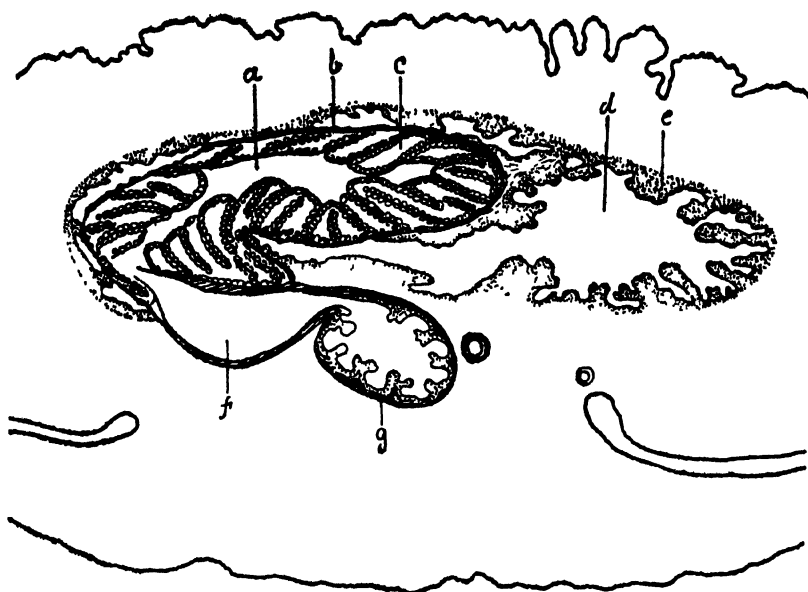


FIG. 38. Section through *pneumo-nephridial* region showing the *ureter* entering the rectum. $\times 25$ (slightly diagrammatic).

a - Inter-nephridial canal. b - Nephridium. c - Nephridial tubule. d - Pulmonary cavity. e - Process of pulmonary wall. f - Ureter canal. g - Rectum.

Regarding the structural interpretation of this gland, there seems to be a difference of opinion amongst previous workers. According to Joyeux Laffaie (1892) the pulmonary chamber is only a modified nephridium. Plate (1893) however regards the pulmonary region and the nephridial gland as two distinct structures, without any relationship between them. Our study of these two organs supports the view of Plate both from the histological and physiological points of view.

(6) REPRODUCTIVE SYSTEM

O. verraculatum is a hermaphrodite pulmonate, possessing both the male and the female genital organs in one and the same individual. There are no separate testes nor separate ovaries, but both these organs are united to form a single gland, known for that reason as the *ovo-testis* or *hermaphrodite gland* (Fig. 39. a). It is rounded and compact in form, brownish in colour, and lies in the posterior region of the body-cavity, just in front of the diaphragm, slightly on the left side. Microtome sections

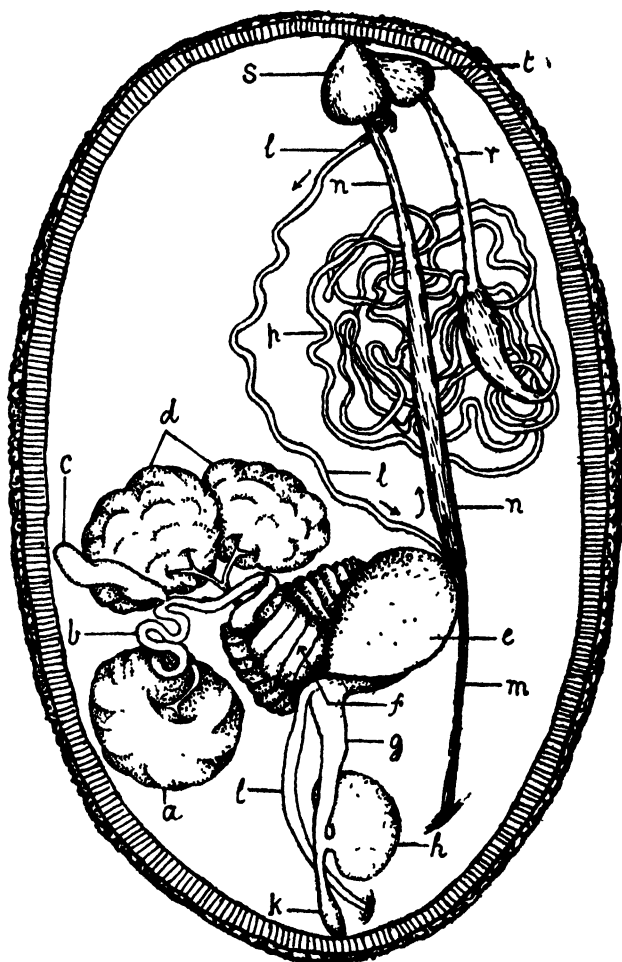


FIG. 39. Dissection of *O. verruculatum* showing the reproductive organs somewhat *in situ*.

a—Hermaphrodite gland. b—Common or hermaphrodite duct. c—Vesicula seminalis. d—Albumen gland. e—Prostate gland. f—Spermoviduct. g—Oviduct. h—Receptaculum seminis. k—Vagina. l—Vas deferens. m—Penial retractor muscle. n—Penis. p—Penial gland. r—Muscular duct of penial gland. s—End-sac of penis. t—End-sac of penial gland containing needle apparatus.

of this gland reveal it to be formed of innumerable follicles containing ova and sperms in their various stages of development (Fig. 40). The follicles containing spermatogonia (c) which give

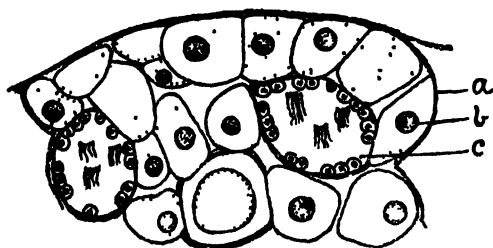


FIG. 40. Section of *ovo-testis* (hermaphrodite gland) showing ova and sperms. $\times 100$.

a—Ovum. b—Nucleus with nucleolus. c—A follicle containing spermatogonia and sperm-bunches.

rise to sperms are generally situated more towards the inner side of the *ovo-testis*, the peripheral region being usually occupied by the ovarian follicles. The ova (a) show conspicuous nuclei, and the sperms are arranged in bunches with small heads and long tails.

From the hermaphrodite gland emerges a narrow and greatly convoluted tube which serves as a common passage for the sperms and ova to pass through, and is therefore known as the *hermaphrodite* or *common duct* (b). On its way it gives off a finger-like whitish vesicle called the *vesicula seminalis* (c) which serves as a store-house for mature sperms. Beyond the origin of this vesiculum, the common duct becomes somewhat thicker in form and passes imperceptibly into a greatly coiled glandular tube, the *sperm-oviduct* (f). The latter divides distally into two unequal tubes of which the thinner one is the *vas deferens* (l) and the thicker one, the *oviduct* (g). The *oviduct* runs posteriorly below the pulmonary chamber, and is met on the way by a small duct from a round vesicle, the *receptaculum seminis* (h), also known as the *spermatheca*. The vesicle contains innumerable sperm clusters moving about in a semi-liquid brownish substance. Posteriorly the oviduct enters the floor of the body-cavity and opens to the exterior on the ventral side, just in the neighbourhood of the anus.

The *vas deferens* (l) runs a short distance posteriorly in company with the oviduct. But instead of opening to the exterior at the posterior end like the latter, it penetrates the floor of the body-cavity, turns cephalad, proceeds anteriorly through the floor-tissue, and emerges again into the body-cavity near the oral end on the right side. It then forms a long coil in the body-cavity and ultimately enters a strongly developed, elongated,

muscular tube called the *penis* (n). The latter leads anteriorly into a swollen muscular sac called the *penial end-sac* (s) which opens to the ventral side at the base of the right tentacle.

The *penis* is a compound muscular tube containing a special type of dentate penial armature. A transverse section of this compound tube (Fig. 41) shows three different tubes or sheaths

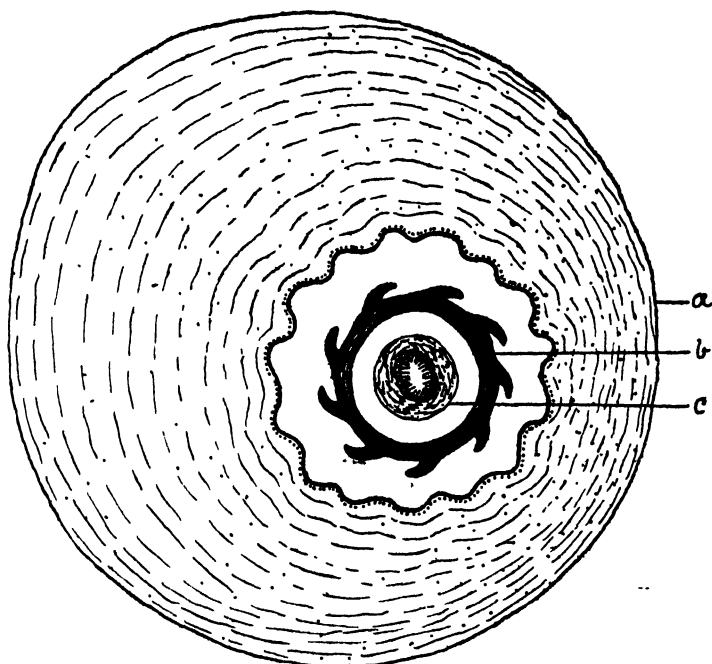


FIG. 41. Transverse section of *penis*. $\times 100$.

a - Outer muscular sheath. b - Middle chondroid sheath. c - Vas deferens.

enclosed one within the other. The *innermost* (c) is the *vas deferens* lined with ciliated epithelium, the long cilia projecting within and almost filling the lumen of the duct. The *middle tube* (b) consists of a thin sheath formed of chondroid substance containing scattered fibres with spindle-shaped nuclei. The peculiarity of this sheath is that it carries serially arranged curved *teeth* or spines on its outer side. The *outermost tube* (a) forms a thick muscular coat having longitudinal folds on its inner wall invested with a thick chitinous lining.

The spiny processes or *teeth* borne on the middle sheath show variation in regard to their size and structure. Those situated in the posterior region of the sheath are not only larger than the anterior ones, but also contain a type of calcareous granules of

irregular shape (a) which are almost absent from the anterior ones (Fig. 42. A, B).

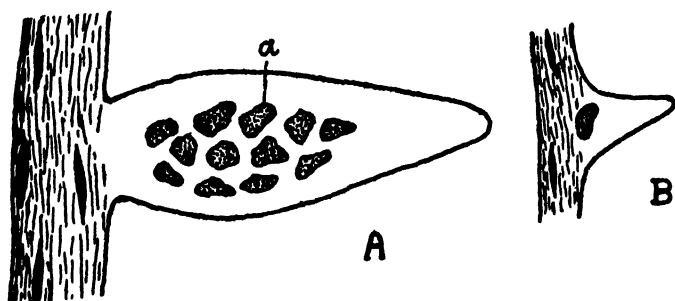


FIG. 42. A:—*Tooth* from the dentate posterior portion of the penial sheath. $\times 1100$.

B:—*Tooth* from the dentate anterior portion of the penial sheath. $\times 1100$. a—Calcareous granules.

The movement of the *penis* is effected by means of a long muscular strand called the *penial retractor* (Fig. 39. m). It is attached at one end to the posterior extremity of the penis, and at the other to the floor far back in the hind region of the body-cavity. It is the retractor muscle whose function is to withdraw the penis after evagination. In the latter process the dentate penial armature, described above, is believed to serve an irritating or itching function (Plate). But it also seems probable that by reason of their reversed arrangement, the curved teeth may be used for gripping the surface of the vaginal opening in order to prevent its slipping out.

In addition to the principal genital organs described above, there are also a few accessory structures and glands developed in connection with the reproductive system of this slug. Associated with the sperm-oviduct, for instance, are found two glandular masses which constitute the so-called *albumen gland* (Fig. 39. d). The gland is somewhat creamy-white in colour and is composed of large irregular lobes formed of secretory cells containing fat-globules. The secretion of this gland is poured into the proximal portion of the sperm-oviduct through a small common duct.

There is another gland, the *prostate gland* (Fig. 39. e) which is associated with the sperm-oviduct. It is also formed of numerous lobules lined with secretory cells with prominent nuclei. It opens into the sperm-oviduct at its distal end by a somewhat longitudinal slit without the interposition of a regular duct.

There is one more accessory structure which is rather closely associated with the male genital duct of this animal. It is known as the *penial gland* (Fig. 39. p). which consists of a very long, greatly coiled, glandular tube forming an intricate network in the right anterior region of the body-cavity. In a specimen of 4.8 cm. long, the penial gland measured more than 24. cm. in length (nearly five times the length of the body.) Posteriorly the gland ends blindly in the body-cavity. Anteriorly it becomes continuous with a strongly developed muscular tube (r) which runs cephalad and enters a swollen sac (t) which communicates with the *penial end-sac* (s) mentioned above. The anterior portion of this muscular tube encloses a remarkable structure, the *needle apparatus* (Fig. 43). It is a deeply yellowish, hollow,

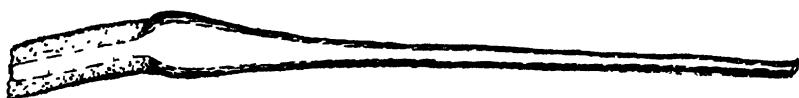


FIG. 43. *Penial needle* showing the central canal communicating with the muscular tube behind. $\times 45$.

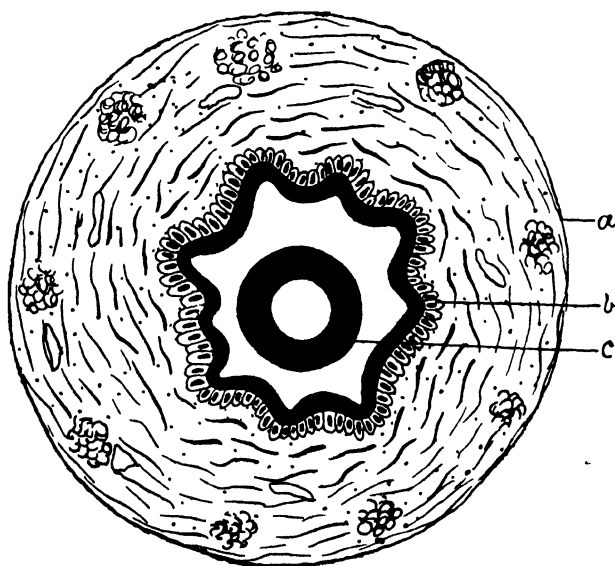


FIG. 44. Transverse section of the muscular tube containing the *needle apparatus*. $\times 300$.

a - Muscular sheath. b - Layer of columnar epithelium, bearing a chitinous lining on the inner wall. c - Needle with the central canal.

chitinous rod having its lumen continuous with that of the penial glandular tube, and opening into the penial end-sac like a syringe needle. *Figure 44* shows a transverse section cut across the muscular tube containing the needle-apparatus.

(7) NERVOUS SYSTEM

The nerve-ganglionic system of *O. verraculatum* is concentrated all round the oesophageal tube behind the posterior end of the pharyngeal mass. It consists of nine nerve-ganglia which are all enveloped within the transparent, vacuolated, cellular tissue described previously in connection with the arterial system of blood-circulation. The several ganglia are as follows :—(a) A pair of buccal or pharyngeal ganglia, (b) a pair of cerebral ganglia; (c) a pair of pleural ganglia; (d) a pair of pedal ganglia, (e) a single unpaired visceral or abdominal ganglion. Excluding the buccal ganglia from the above list, all the rest are situated around the oesophagus, forming thus a definite ganglionic nerve-ring round the same.

Figure 45 shows the ganglionic mass and the principal nerves in *O. verraculatum*. The buccal and cerebral ganglia in that figure are coloured black, pleurals are red, pedals green, and the visceral blue. The numbers and letters relating to nerves are marked in such colours as correspond to those of the ganglia from which they are given off.

The *buccal* ganglia (*black-small*) which are relatively small are situated on the dorsal side of the pharyngeal bulb just behind the oesophageal opening. They are joined to each other by a short median commissure. Each buccal ganglion is connected with the corresponding cerebral ganglion by means of a long slender connective called the cerebro-buccal commissure (d, 1). The cerebrals, the pleurals, the pedals, and the single visceral form together what is called the nerve-ring round the oesophagus. The dorso-lateral corners of this ring are occupied by the *cerebral* ganglia (*black-large*). Laterally are situated the *pleurals* (*red*) of which the right pleural is placed somewhat latero-ventrally. The *visceral* (*blue*) which is a large unpaired ganglion lies, correspondingly, in the ventro-lateral corner of the ring on the left side. The *pedals* (*green*) which are ventral in

Black-coloured (small) — Buccal ganglia and nerves
 " " (large) — Cerebral ganglia and nerves.
 Red-coloured — — Pleural ganglia and nerves.
 Blue-coloured — — Visceral ganglion and nerves
 Green-coloured — — Pedal ganglia and nerves.

position are situated slightly in front of the nerve-ring proper, though closely connected with the same.

The cerebrals are connected with each other by a thick commissure, the supra-oesophageal commissure, which forms the dorsal arch of the nerve-ring. There is another, rather slender commissure connecting the two cerebrals ventrally, which passes underneath the oesophagus, and is therefore known as the sub-oesophageal commissure. Laterally each cerebral ganglion is joined to the corresponding pleural by a cerebro-pleural connective. The pleural ganglia in turn are connected with the visceral by the pleuro-visceral connectives. Of the latter the right connective which is longer and more strongly developed than its corresponding mate, forms the base of the nerve-ring, the visceral ganglion being rather asymmetrically placed on the left side. The pedal ganglia which are joined to each other by a pair of pedal connectives, are connected with the pleurals and the cerebrals by the pleuro-pedal and cerebro-pedal connectives respectively. It may be noted here in passing that the aortic

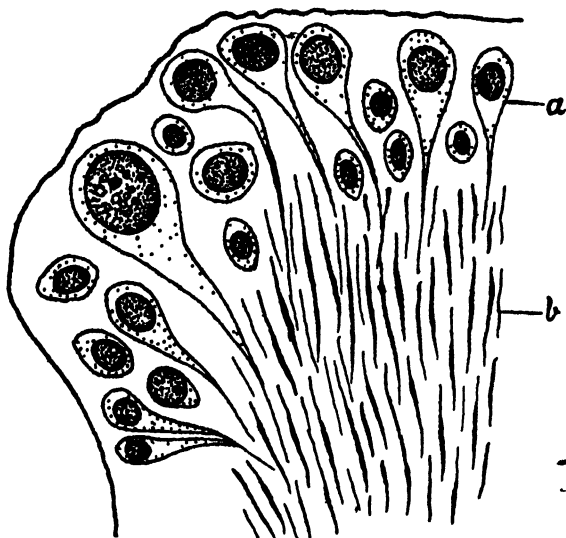


FIG. 46. Section of a *nerve ganglion* showing ganglionic cells (a) and nerve fibres (b). $\times 230$.

trunk, on approaching the nerve-ring, passes forward between the pedal commissures and the viscero-pleural connectives.

An examination of one of the nerve-ganglia under the low power of the binocular microscope shows it to have a granular or slightly tuberculate surface. Microtome sections of the same (Fig. 46) reveal that the granular appearance of the ganglionic mass is really due to the presence of ganglion cells (a) which are extraordinarily large and have very conspicuous nuclei. These cells are situated more towards the periphery, abutting on the surface, and thus giving it the granular appearance. The central portion of the ganglion is occupied by a fibrous tissue intermixed with nerve fibres (b). The ganglion cells are usually unipolar, the long thread-like process of each being directed towards the central mass of nerve-fibres. *Figure 47* is the diagram of one of the largest ganglion cells magnified to about five hundred times of its original size.

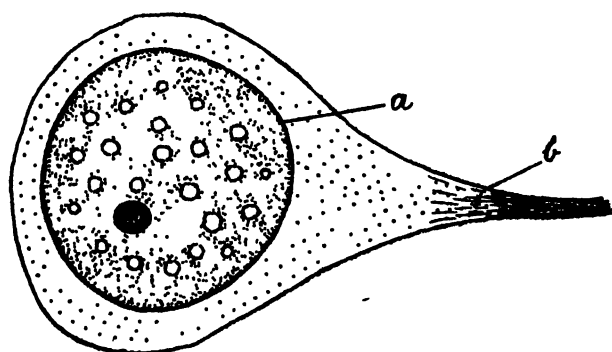


FIG. 47. A unipolar *ganglionic cell*. $\times 500$.

a - Nucleus. b - Cell-process or fibre.

Dissection of the pedal ganglia reveals the presence of a whitish body called the *otocyst* located within the right ganglion. It is somewhat oval in form, and has one end jutting out from the posterior side of the ganglion in question. At the other end the *otocyst* lies embedded within the central fibrous tissue of the ganglion. *Figure 48* gives a transverse section of the right pedal ganglion, with the *otocyst* (a) cut across in the middle and containing minute calcareous bodies designated by Watson (1926) as *otoconia*.

Watson (1926) states to have found two *otocysts*, one in each pedal ganglion of *Oncidiella*. He also mentions that each *otocyst*

is innervated by a small nerve coming from the cerebral ganglion. Our studies of *O. verraculatum* however reveal the presence of only a single otocyst, and that too located in the right pedal ganglion.

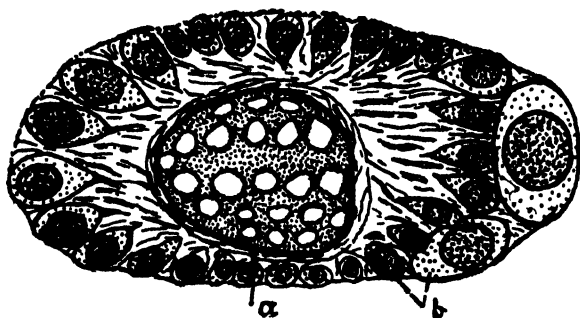


Fig. 48. Section of the right pedal ganglion. $\times 175$.

a — Otocyst. b — Ganglionic cells.

Nerves and their distribution. (Fig. 45):—*Buccal nerves.*—Each buccal ganglion gives off three main nerves of which two run anteriorly, while the third takes a lateral turn. Nerve (b) innervates the muscles surrounding the oesophageal opening. Nerve (c) controls the dorsal and lateral muscle-bands forming the wall of the pharyngeal bulb. Nerve (d) descends latero-ventrally and joins the cerebral ganglion, thus constituting the cerebro-buccal connective. On its way it gives off two branches of which one (d_1) goes to the pharyngeal muscles, and the other (d_2) to the salivary gland. In addition to the buccal nerves, the buccal commissure sends inwards a median unpaired nerve (a) which goes to the radula-papilla.

Cerebral-nerves.—Each cerebral ganglion gives off five principal nerves, all directed anteriorly. Besides these, the right cerebral ganglion sends out one more nerve, on that side. Number (1) is a long slender nerve which ascends upwards, meets the buccal ganglion and thus constitutes the cerebro-buccal connective. Number (2) is a strong well-developed nerve which innervates the ventral anterior and posterior protractors of the pharynx. It is distributed at the basal region of these muscles. Number (3) is another strong stout nerve which breaks into two branches both of which enter the body-floor between the buccal tube and the penial end-sac, and innervate the labial palp and the sense-organs situated on that side. Number (4) is a thin slender

nerve which goes to the dorsal anterior protractors of the pharynx. Number (5) is a strongly developed nerve which goes to the tentacle and the cephalic eye. Number (6) is a nerve which is given off only from the right cerebral ganglion. Shortly after its origin it divides into two branches. The anterior branch divides again into two sub-branches of which one goes to the penial end-sac, and the other to the muscular tube of the penial gland. The posterior branch gives off a small nerve to the penial retractor muscle and another to the vas deferens and the penial gland.

Pleural nerves.—Each pleural ganglion sends off three strongly developed nerves which innervate the anterior (x), the lateral (y), and the posterior (z) regions of the mantle on each side. Nerve (z) on the left is rather short, but its mate on the right side takes a longer course, runs posteriorly along the genital artery, then turns outwards, passes below the pericardium and innervates the adjoining postero-lateral region of the body-wall.

Visceral nerves.—The visceral ganglion gives off two strongly developed long nerves. Nerve (A) runs straight posteriorly along the genital artery and breaks into two branches beneath the pneumo-nephridial region. These branches enter the body-wall on either side of the rectum and innervate the area of the foot-hyponotum. Nerve (B) is the most important visceral nerve. After running for a short distance along the aorta it divides into two branches (B_1 , B_2). (B_1) follows the course of the genital artery and innervates the various genital organs. On its way it gives off a branch on the right side which enters the foot in the corner between the diaphragm and the pericardium. (B_2) runs along the digestive artery and sends off branches to the liver and the digestive organs.

Pedal nerves.—Each pedal ganglion gives off six nerves all of which are concerned with the innervation of the foot-organ. Nerve (I) arises from the antero-ventral side of the ganglion and enters the foot in the region of the pedal gland, situated just in front. Nerves (II, III, IV) are rather thin and slender, which arise laterally and innervate the lateral portions of the foot. Nerve (V) is strongly developed, which runs posteriorly and enters the foot in the posterior region. On the way it gives off a small branch which bifurcates before penetrating the pedal tissue. Nerve (VI) arises from the postero-ventral side of the ganglion. It directly penetrates the floor of the body-cavity and innervates the adjoining foot-region.

(8) ORGANS OF SENSE

The organs of sense found in *O. verraculatum* consist mainly of those concerned with the sensation of touch and of vision. Eyes which form the organs of vision, are borne on the tentacular tips and dorsal tubercles, while tactile organs are located in the surface of the tentacles and the oral lappets.

Eyes.—The eyes in *O. verraculatum* are situated in two different regions and consist of a large number carried by each specimen. One pair of them is situated at the tips of the tentacles. They are known for that reason as tentacular or *cephalic eyes* (Fig. 1. e). Besides these, there is a large number of others which are arranged in groups, and borne by some of the dorsal tubercles. They are therefore known as *dorsal* or *mantle eyes* (Fig. 1. me.). These ocular groups generally consist of 3-4 eyes in each, though in one case there were 6 eye-spots arranged on the flat top of a single tubercle. The number of these dorsal eyes is usually large, and the examination of several specimens gave the maximum number of 54 in one of them. Semper (1906) found 98 on one from the large number of specimens he had examined.

The cephalic and the dorsal eyes of this slug differ from each other not only in respect of their location, but also in their structure and probably function. The *structure* of the *cephalic*

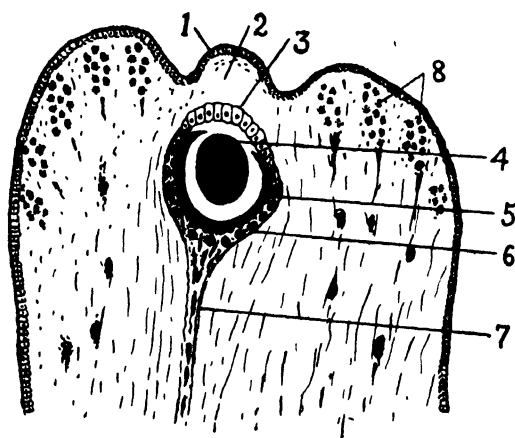


FIG. 49. Longitudinal section through the *tentacular eye*. $\times 60$.

- 1—Epidermis. 2—Open space between the epidermis and cornea.
3—Corneal layer. 4—Lens. 5—Pigment layer. 6—Retinal layer
7—Optic nerve. 8—Tactile sense organs.

eye is as follows:—(Fig. 49). The eye, instead of projecting directly on the tentacular surface, is sunk slightly below the epidermal layer of the tentacular tip. The various structures associated with the cephalic eye, from without inwards are: (1) the epidermal layer formed of columnar epithelium, (2) an irregular empty space situated between the epidermis and the eye-ball, (3) the corneal layer of the eye formed of transparent cells with central nuclei and columnar in form, (4) the oval lens situated in the eye-ball cavity, (5) the cup-shaped layer of pigment cells lining the eye-ball cavity, (6) the retinal layer of visual cells connected basally with the sensory fibres of the optic nerve (7).

The dorsal eye (Fig. 50), on the other hand, is constructed after the model of the Vertebrate eye, and *differs* from the cephalic

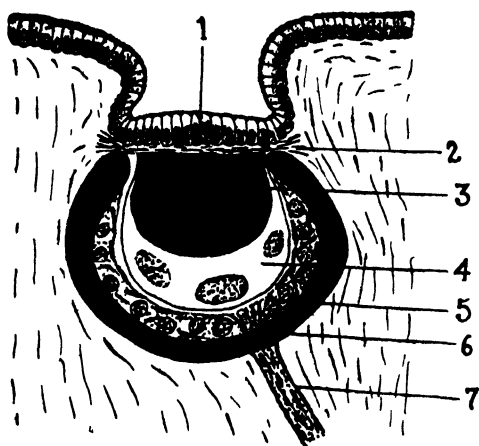


FIG. 50. Longitudinal section through the *dorsal eye*. $\times 280$.

1—Epidermis (pseudocornea). 2—Subcorneal tissue. 3—Lens "principal". 4—Lens "accessory". 5—Retinal layer. 6—Pigment layer. 7—Optic nerve

eye in several respects. The main difference lies in the relative positions of the pigment and retinal layers which, in the case of the dorsal eye, are reversed. Here the pigment layer (6) surrounds the retinal-layer which forms its inner lining, with the result that the optic nerve (7) has to penetrate the pigment-cup before it can spread its fibrous elements in the retinal tissue. Another point of difference lies in the structure of the lens which in the case of the dorsal eye consists of two distinct portions: One anterior hemispherical portion

called the "principal" lens (3), and a posterior cup-like or crescentic one called the "accessory" lens (4). The accessory lens shows three to four large and conspicuous nuclei in its substance, and occupies the position corresponding to the vitreous humour of the Vertebrate eye. A third point of difference between these two types of eyes relates to the morphological nature of the corneal layer which in the case of the dorsal eye is a direct continuation of the epidermal layer, and is known for that reason as pseudocornea. Unlike the cephalic eye, the dorsal eye thus opens directly on the surface of the dorsal tubercle. Between the pseudocornea and the lens of the dorsal eye intervenes a thin layer of connective tissue fibres, known as the subcorneal tissue (2), not found in the cephalic eye.

According to Semper the dorsal eyes are specially adapted to the stimuli of light and shade, and to that extent they differ in function from the cephalic eyes which serve as the normal visual organs of this slug.

Tactile organs.—Organs of tactile sensation are situated on the tentacular tip surrounding the cephalic eye and also on the oral lappets. They consist of a peculiar type of sensory cells with conspicuous nuclei (Fig. 49. 8; Fig. 51. 2), arranged in groups, situated just below the epidermal layer and connected

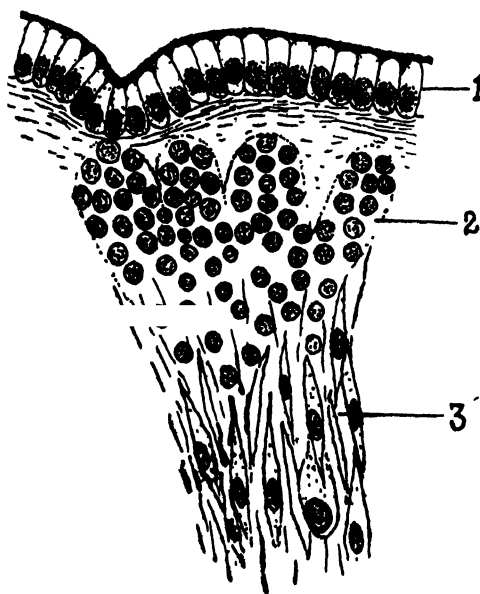


FIG. 51. Longitudinal section through *tentacular tip*. $\times 500$.
1—Epidermis. 2—Tactile sense organs. 3—Nerve fibres and ganglion cells.

basally with bipolar ganglion cells. According to Plate (1891-93) these cell-groups possess a high degree of tactile sensitiveness. The slightest contact with the tentacular tip brings forth an immediate reaction resulting in the withdrawal of the same within the tentacular stalk. When the disturbance ceases, it is slowly evaginated and drawn out to its full length. The tactile irritability of the lappets is also great, and they are always seen engaged in feeling their way over the substratum on which the animal is creeping.

(D) HABITS, HABITAT AND DISTRIBUTION

O. verraculatum is a species of marine slugs, found usually along the intertidal zone, in nooks and crevices of the coastal rocks bordering creeks and inlets of the sea. These slugs creep out of their crevices and bathe themselves in the rising tide, and retreat again to their rocky shelters when the water recedes. In their general colouration they can hardly be distinguished from the greyish or slaty colour of the rocky surroundings in which they live and move about. Their mode of locomotion is by creeping along the substratum by means of the ventral fleshy foot which forms the principal organ for that purpose. Their food consists mainly of sandy detritus which is taken in at the mouth and passed out at the anus. The organic particles including various kinds of algæ contained in this sandy mass are digested on their way down the alimentary canal and absorbed into the blood-system of the animal. It is usually in the monsoon that these slugs lay eggs, enveloped in a large gelatinous mass and attached to a rocky substratum nearby. The life-history involves a free swimming larval stage (veliger larva) which shortly afterwards metamorphoses into the typical adult form.

Zoo-geographically, these slugs are distributed along the western coast of India, and specimens of different sizes have been collected from such places as Vengurla, Malwan, Bombay and Kathiawar ports. Outside the Indian limits they are found, according to Semper, "along the shores of N. Australia and the western portion of the Pacific, in the whole of the Chinese sea as far as Japan, in the Indian Ocean and the Malayan Archipelago and on the east coast of Africa."

One of the most outstanding characteristics of these slugs is the presence of the so-called *dorsal eyes* found on their back. In fact their presence has been noted in almost all the genera

coming under the family *Oncidiidæ* to which these slugs belong. As has been described before, these eyes are perfect visual organs turned upwards in various directions and constructed rather remarkably on the Vertebrate model. Their location on the back of these creatures, their presence almost exclusively in the family *Oncidiidæ* of the whole animal kingdom, and the perfectness of their structure: all these points combine to indicate that these eyes have originated in these creatures quite independently, and that they must have some definite purpose to serve. Semper (1906), who has made special observations on the mode of life and habits of these slugs, suggests that these visual organs, situated as they are on the back of the animal, are keenly sensitive to changes in "light and shade," and as such quite indispensable to the organism concerned. The idea behind this suggestion is based upon certain anatomical and ecological facts which it is desirable to note down briefly, so that their significance may be properly measured.

One of these facts relates to the presence of innumerable mucous glands, both unicellular and multicellular, situated all over the dorsal and peripheral surface of the mantle of these slugs. The secretion of these glands is supposed to be in some way "injurious or offensive" to intruders and enemies, which thus affords these slugs the only means of defence against outside intrusion or danger, in an otherwise helpless condition. According to Semper the probable enemies of these slugs are two genera of fishes—*Periophthalmus* and *Boleophthalmus*, known commonly as mud-skippers, which indiscriminately feed on these slugs, and which in their zoo-geographical distribution follow closely in the wake of these *Onchidium* slugs.

The presence of eyes and mucous glands on the dorsal surface of the mantle, the distribution of these slugs running parallel to that of the two genera of fishes mentioned above, and the predatory relationship of the latter with the former: these facts have led Semper to advance an interesting theory explaining the *modus operandi* and the significance of the dorsal eyes of these slugs. His hypothesis in his own words runs as follows:—"The hunting *Periophthalmus* approaches the slug suddenly with rapid leaps. It rises several inches into the air and may thus not infrequently throw a shadow from some distance off, on the back of the slowly creeping *Onchidium*, and of course alarms it greatly. The mollusc has its eyes turned upwards in various directions. Suddenly aware of the fish or of its shadow, it quickly draws up its body, thus contracting the glands in the skin on all sides, and

then discharges the poisonous mucous secretion into the air towards the pursuing fish. The fish now alarmed on its part, and hit by the shower of minute shots which may be in some way injurious or offensive, retires from the pursuit and the *Onchidium* is safe." That is how the dorsal eyes, keenly sensitive to the changes in light and shade, play their part in the life-economy of these slugs. Semper admits that this is merely a hypothesis though he qualifies it as being an extremely probable one, in view of the peculiar anatomical and ecological facts recorded above.

Observations made by other investigators do not however corroborate the views advocated by Semper. Bretnall (1919), in his report on the *Oncidiidae* from Australia and South Western Pacific Islands, states that the species of *Oncidiidae* found by him in these regions possessed the so-called mantle eyes in a well-developed form, but the areas in which these slugs were found, were completely devoid of any *Periophthalmus*-like fishes. Aray and Crozier (1921) who also have made a special study of the *Oncidium* species from Bermuda, remark in the same style as Bretnall, in respect of the presence of dorsal eyes and parallel distribution.

Our observations made along the western coast of India and particularly along the Bombay island, have been partly positive and partly negative. Three species of these slugs are found in several areas of the island-shore, which are (1) *Oncidium verraculatum*, (2) *Oncidium simrothi*, (3) *Oncis martensi*. Of these *O. verraculatum* which is the largest amongst them has been observed to inhabit rocky places along the shore, in nooks and corners, and under stones—areas absolutely devoid of any species of the so-called mud-skipper. The other two species, on the other hand, are invariably found in muddy places along the shore which are also rich in the presence of the *Boleophthalmus* fish. All the three species, regardless of the difference in their habits, and in their zoological associations with the mud-skipper, possess the dorsal eyes on their back with a perfectly developed structure.

According to Aray and Crozier (1921) the dorsal surface of these slugs possesses an exclusive photic irritability, and the dorsal eyes are the chief specialised organs of photo-receptors. These workers have also found experimentally that the mantle glands do not discharge their poisonous secretion under the stimulation of "light and shade," and that it is only the tactile excitation which is pre-eminently successful in effecting the discharge

from these glands. Animals of the type of the Isopods, crabs, chitons, etc. which frequent the intertidal zone, often come in contact with *Oncidium* specimens, and in the course of such contacts there occurs an immediate discharge of the fluid from these glands, followed by the retreat of those intruders.

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STUDIES IN THE ECOLOGY OF MANGROVES

1. DETERMINATION OF OSMOTIC PRESSURE OF *AVICENNIA ALBA*, BLUME*

(With six figures and six tables in the text)

By

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Science, Bombay.*

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INTRODUCTION

The osmotic pressure of the cell sap from the leaves of mangrove vegetation depends upon the sodium-chloride content of the sap, and the sodium-chloride content is an important factor in the distribution of the plants which grow in salt marshes. Hence the determination of osmotic pressure is important, and essential from the ecological point of view, as it forms one of the main factors in the ecology of the salt marsh vegetation.

Drabble and Lake (15) used the plasmolytic method of de Vries (13) to determine the osmotic strength of the cell sap in plants growing in different environments. According to them, mesophytes in general have a lower osmotic strength in the cells than xerophytes; but this characteristic does not aid in retarding the loss of water, and is meant for absorbing water through the leaves. Drabble and Drabble (14) further studied the relation between the osmotic strength of the cell sap in plants and their physical environment. They came to the conclusion that the plants which have most difficulty in obtaining an adequate supply of water, have a higher concentration of cell sap than those which are more favourably situated. This higher concentration of cell sap retards evaporation of water, lowers the freezing point of the sap, and increases the absorption of water.

**Avicennia alba*, Blume is retained by me as specifically different from *A. officinalis*, Linn. on the authority of Th. Cooke and K. Biswas (3).

The above results were confirmed by Hill (18) when he studied the osmotic properties of the root hairs of salt marsh plants. According to him the degree of salinity in any one spot is not constant, obviously depending on the tides. The tides are often sufficiently high to flood the whole area, but they may also be so low as to cover none of the parts under vegetation. A region which is covered only by the highest tide becomes increasingly saline during the intertidal cycle, especially during the periods of relative drought; and all localities are less saline after rain. The effect of the rain is to wash out the salt from the soil. Hill further found out that the osmotic strength of the cell sap of the root hairs varies with the concentration of the surrounding medium, being lower when the external solution is weaker, and greater when the concentration of the surrounding solution is higher. The root hairs of *Salicornia*, growing in places where the soil solution is strongly saline, can accommodate their internal osmotic pressure to the changes in the salinity of the water of the surrounding medium. In any area the osmotic strength varies with the physiological scarcity of water, that is water which is not available to the plant due to its saline nature. In all plants growing under the same conditions the osmotic strength of the cell sap is generally the same.

Halket (16) while working on the absorption of water by the aerial parts of certain salt marsh plants found that some typical examples, like *Salicornia* sp., especially under conditions of drought, are capable of absorbing water through the epidermal cells of their aerial parts, not only from precipitated atmospheric moisture, but also from a salt solution approximating in strength to that of the sea. Further the author found that the amount of water absorbed in this way can in no way replace normal absorption. Again Halket (17), when studying the effect of salt on the growth of *Salicornia* has found that *S. Oliveri* Moss. and *S. herbacea* Linn. grow better in the presence of sodium chloride than in its absence, the greater growth being when 2 to 3 per cent of this salt is present. The presence of a large amount of sodium-chloride, as seen from the pan experiments, can be resisted by *Salicornia herbacea* and *Suaeda maritima* Dum.

Similarly Delf (12) while studying transpiration in succulent plants came to the conclusion that the water stored may be of value in avoiding the evils of a fluctuating water supply as in many rock plants, or it may be a provision against temporary rapid transpiration as in the Mangrove Swamps of Ceylon. It is further stated that the storage tissue may appear as a permanent

characteristic of plants which are found exclusively in saline situations. The same author (11) further showed in her work on "Transpiration and behaviour of stomata in Halophytes" that *Salicornia herbacea* and *Suaeda maritima*, both typical halophytes, have a high rate of transpiration per unit of surface area. This area may be equal to or even greater than that of typical mesophytes. The power of stomatal movement in *Salicornia* appears to be lost after the flowering period whose stomata then remain permanently closed. In the case of *Aster Tripolium* Linn. the stomata were also sensitive to the relative humidity of the atmosphere.

Blatter (4) in his paper on the Mangrove of the Bombay Presidency and its Biology, gives a list of Mangrove species found in the Bombay Presidency with their characteristic morphological and anatomical features. According to him the peculiarity to be noted in all mangrove vegetations consisting of different families and species is that : they have coriaceous leaves, a shining surface, entire margins (excepting *Carapa obovata* Bl. with pinnate leaves), and uniform internal structure.

Chapman (8) who studied the halophytic problem in the light of recent investigations came to the conclusion that a number of environmental factors including the season of the year are involved. It is also necessary to know the phase in the life cycle involved. He quotes Bergerlandefeldt's (2) work on dune and salt marsh halophytes, which concludes that the osmotic pressure of the cell sap is dependent upon the salt concentration in the soil solution.

According to Adriani (1), osmotic pressure of the cell sap is higher in plants growing in the more saline soils, and can be correlated with the salt content of the soil. It fluctuates with the rainfall, being higher in dry weather and lower in wet weather ; the variations are in general an expression of the displacement in the water content, with no relation to the external conditions. The osmotic pressure may vary from 13 to 48 atms. The osmotic pressure of the cell sap is due to the soluble salts contained in it, and from Adriani's data it can be seen that the sodium chloride component may vary from 18 to 85 per cent of the total osmotic pressure.

METHODS

Cooper and Pasha (9, 10) while studying the suction force of the mangrove cell sap, found the osmotic values of the leaves of *Avicennia officinalis* Linn., *Acanthus ilicifolius* Linn. and *Senneratia apetala* Ham. by the plasmolytic method only.

In the present investigation for the determination of osmotic values, the freezing point method was used. The plasmolytic method was tried, but it was found that the range of variations of the concentrated sugar solutions was very wide, and even with all due precautions the results obtained were not so accurate and reliable as found by the freezing point method. Our findings confirm the results obtained in recent investigations by several workers in Europe: H. Walter (21), A. Buhmann (7) and Braun-Blanquet (4). The following table given by Walter (21) wherein he also compares the results obtained by the plasmolytic and cryoscopic methods, shows very perceptible differences between the two methods.

TABLE 1

	O. P. by Plasmolysis		O. P. by Cryoscopy
	in sugar solution	in salt solution	
1. <i>Zebrina pendula</i> , Schnizl	4.23	4.48	5.17
2. " " "	4.12	4.65	6.42
3. " " "	4.19	4.70	5.71
4. " " "	4.21	4.57	5.29
1. <i>Iresine Herbertii</i> , Hook.	-6.72	7.08	8.30
2. " " "	6.50	7.10	9.44
3. " " "	6.94	6.81	7.98
4. " " "	6.33	6.92	8.02

Walter (21) further shows that the error in the values derived by the plasmolytic method may even amount to 100 per cent. He has recently stated also that the plasmolytic method is unreliable. For similar reasons Braun-Blanquet and Walter (6) have used the cryoscopic method.

Buhmann (7) in her recent investigations also showed that the plasmolytic method is not so reliable as the cryoscopic one.

It was therefore decided to use in the present investigation the cryoscopic method of determining the osmotic pressure in preference to the older method of plasmolysis.

TECHNIQUE

The mangrove leaves of *Avicennia alba* Bl. were collected in special unbreakable glass tubes with corks fitted in air-tight aluminium boxes. For this purpose only normal healthy leaves were chosen. After bringing to the laboratory the boxes were put in boiling water for twenty minutes. This was done with a view to killing the plant material as quickly as possible in order to prevent any alterations taking place in the tissues. A suitable method, according to Walter, of killing the plant material is to

heat the tissues to 100°C , which also destroys the enzymes and partially sterilises the tissues. In the present case the heating was done in a boiling water bath. The aluminium boxes were placed erect in the boiling water, which, however, was not allowed to reach up to the lids, in order to prevent its getting inside the boxes. After cooling, the cell sap was extracted from the leaves by means of a special silver-plated brass-extractor and was collected in a test tube.

The freezing point of the cell sap was determined by a special thermometer ("Prolabo"), having each degree divided into 100 parts. The usual precautions were taken and the error of the thermometer was determined by using distilled water. The apparatus was arranged as shown in Fig. 1. The cell sap

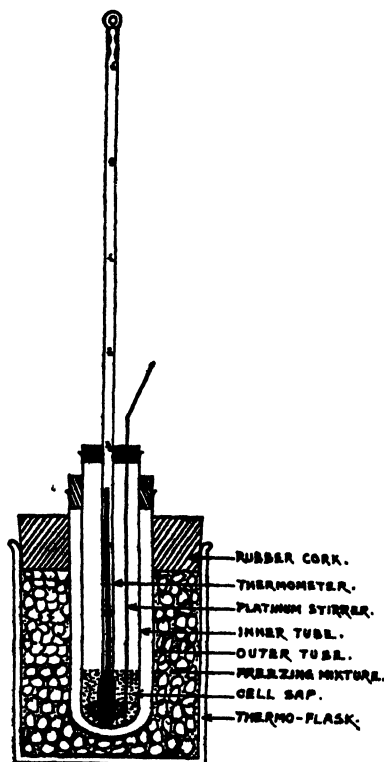


Fig. 1

was put into a test tube and the thermometer was inserted in it. A platinum stirrer with glass handle was kept also in the tube to stir the liquid. The tube was protected by another glass tube into which it fitted loosely. These tubes were placed in a

thermo-flask containing a freezing mixture. The level of the mercury column began to fall and reached a certain mark. Then as the liquid began to freeze it gave off heat and the mercury column rose and remained stationary. The point where mercury remained stationary, gave the freezing point of the cell sap. For each determination, including even the error of the thermometer, three readings were always taken and their mean noted. From the mean reading of the freezing point, the osmotic pressure was calculated by using the following formula:—

$$T - T_1 \times 12.05 = \text{Osmotic pressure.}$$

where T represents the freezing point of distilled water, and T_1 that of the cell sap, and 12.05 is the ratio of the osmotic pressure expressed in atmospheres to the freezing point depression in degrees centigrade of a solution of normal solute in distilled water.

We can illustrate this by quoting a concrete example of the cell sap of the leaves collected on 23rd September 1937. The mean freezing point was found to be -1.8016°C and the mean error of the thermometer was $+0.0300^\circ\text{C}$. Hence $T = +0.03$ and $T_1 = -1.8016$, therefore $T - T_1 \times 12.05$

$$= (0.03) - (-1.8016) \times 12.05$$

$$= 1.8316 \times 12.05$$

Therefore osmotic pressure = 22.0708 atmospheres.

Similarly determinations were made for samples of sea water collected together with the leaf samples of the mangrove. The samples of the mangrove leaves and sea water were collected during one year, the time of collection being generally just before or after the low tide, that is to say, the collections were made about the time when the tide was at its lowest (*cf.* tide graph fig. 2).

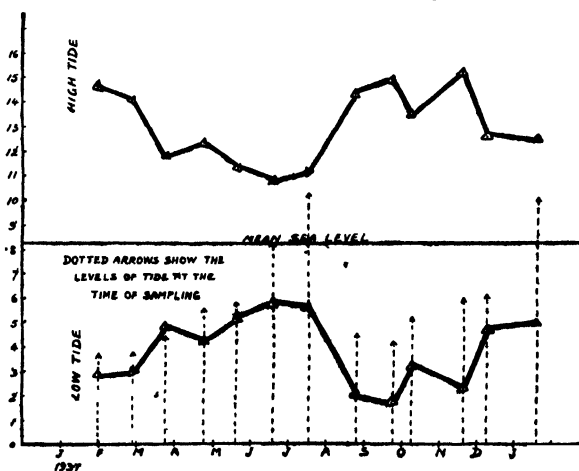


Fig. 2

RESULTS

The osmotic pressure of the cell sap of the leaves of *Avicennia alba* Bl. is given in the following table together with that of the sea water. Leaf samples were chiefly collected from the Colaba reclamation area, which is near the Botany Laboratory of the Royal Institute of Science where these investigations were carried out :—

TABLE 2

Date	Time of collection of samples	O. P. of cell sap of leaf of <i>A. alba</i> Bl.	O. P. of Sea water
27—2-37	8-15 A. M.	27.305 atms.	26.259 atms.
22—3-37	3-10 P. M.	32.770 "	25.420 "
22—4-37	3-25 P. M.	34.010 "	26.654 "
18—5-37	12-50 noon	37.294 "	26.871 "
18—6-37	12-55 noon	27.269 "	22.591 "
15—7-37	2-50 P. M.	26.112 "	15.146 "
23—8-37	8-7 A. M.	34.788 "	17.721 "
23—9-37	8-15 A. M.	22.071 "	15.092 "
7-10-37	7-49 A. M.	33.788 "	24.148 "
19-11-37	7-47 A. M.	34.744 "	25.706 "
8-12-37	8-25 A. M.	43.340 "	25.706 "
18—1-39	9-30 A. M.	55.144 "	26.345 "
Average		34.016 "	23.138 "

It will be seen from these results that on the average the osmotic pressure of the mangrove leaf cell sap is 34.016 atms. and that of the sea water 23.138 atms. The fluctuation in the value ranges in the case of the leaf cell sap from 22.071 to 55.144 atms. and in the sea water from 15.092 to 26.871 atms. The wide variation in the osmotic pressure of the leaf cell sap may be attributed to the different times of collecting the samples as the samples were collected some times just before the low tide and some times just after, and it is probable that the concentration of the cell sap may have varied, causing thereby the fluctuations in the osmotic pressure. That this explanation is true can be seen from the experiment of 12-12-38 in which the following results were obtained :—

TABLE 3

	Low tide	High tide
Osmotic pressure of the leaf cell sap of <i>Avicennia alba</i> Bl. ...	36.682 atms.	46.754 atms.
Osmotic pressure of the sea water ...	27.787 „	27.450 „

This is true much more for the cell sap than for the sea water. The reason given above can be applied to sea water also, as when the tide is at its low ebb, the concentration increases more than at the time of the incoming tide and hence we see fluctuations also in the result of the osmotic pressure of the sea water.

It is for these reasons that the average values of leaf cell sap and sea water are calculated in both the cases. It will be interesting to note that Walter (23) also obtained similar results in his investigations on the mangrove vegetation of East Africa.

From the following table it is clear that the values obtained for the osmotic pressure of the leaf cell sap in the case of *Avicennia alba* Bl. are higher than those obtained for *Sesuvium Portulacastrum* Linn. and *Aeluropus repens*, Parl.

TABLE 4

Osmotic Pressure of the leaf cell sap in atms.				
Date	Expt.	<i>Avicennia alba</i>	<i>Sesuvium Portulacastrum</i>	<i>Aeluropus repens</i>
7-2-37	1	27.30	20.07	10.80
13-3-37	2	32.80	30.70	14.05

This fact of higher osmotic pressure in the case of *Avicennia* has been also recorded by Walter (25).

Further it must be pointed out that the average for the monsoon season i.e. from June to September amounts to 27.56 atms. for the cell sap and 17.637 atms. for the sea water. Similarly the averages for the remaining months i.e. from October to May are 37.299 atms. for the cell sap and 25.888 atms. for the sea water.

DISCUSSION

The osmotic value of sea water at Colaba is on an average 21.631 atms., the lowest being 15.09 atms. and the highest 26.87 atms. Similar findings have been recorded by Walter (25)

together with the facts that the osmotic values of the mangrove roots and leaves are very high, and that fluctuations in them are also found with high and low tides. According to him the osmotic value of the water of the Indian Ocean amounts to about 24 atms.

Also in East Africa, according to Walter (23) the fluctuations in the osmotic values in *Rhizophora* sp. and *Avicennia* sp. are enormously high, and those for the leaves are always greater than those for the soil solution.

The high fluctuations are due in some respects to high and low tides, as mentioned above, or are seasonal in character. That they are due to high and low tides can be seen from the experiments of Walter (25) and our own (Table 3). That the fluctuations are also due to different seasons can also be seen from Table 2 showing that the lowest osmotic pressure is in the month of July 26.11 atms. and the highest in the month of January 55.144 atms. These results can be explained by the fact that during monsoon due to the dilution of the cell sap the osmotic pressure falls whereas during the cold season transpiration decreases and therefore the osmotic pressure of the leaves rises.

Steiner (20) is of the opinion that $\frac{2}{3}$ of the osmotic pressure of the East African mangroves is due to the chlorine content of the leaves and in this respect mangroves are not different from other halophytes. The difference between the osmotic values in leaves and soil solution in the case of *Avicennia* sp. is 20 atms., and in other parts like roots, shoots, etc. it is only 8.9 atms., and this probably is sufficient to explain the rise of cell sap as the roots are always wet and evaporation is low (i.e. not exceeding 1 cm. per hour), and the intensity of transpiration (except in *Avicennia*) is also low and equal to that of conifers in Europe.

Similarly Walter (24) while studying the ecological conditions of a bog desert of Namib, found that the halophytes collect a lot of salt in the succulent leaves and stems. The osmotic values are high and are over 30 atms.

It will be seen from the Table 2 that on the whole the osmotic pressure of the leaves is high throughout the year, and this is borne out also by the studies of Walter and Steiner (25). Also these values are higher than those of the sea water and this again is borne out by the experiments of the same workers. The constant for the sea water is about 23 atms. in Tanga Bay as found by Walter (25). No differentiation is made in the physico-chemical constituents of the young and adult leaves. The leaves are generally covered with water at high tide ; they are succulent,

and have a higher chlorine content. From the Table 5 given below the different osmotic values given by Walter (25), myself and Sen Gupta (19) in different zones of mangroves will be seen.

TABLE 5

		Walter	Author	Sen-Gupta
<i>Sonneratia alba</i>		31.45 atms.		
<i>Sonneratia apetala</i>			45.465 atms.	14.99 atms.
<i>Rhizophora mucronata</i>		31.6 atms.	33.788 "	32.13 "
<i>Coriops Candolleana</i>		32.45 "	29.438 "	26.65 "
<i>Avicennia marina</i> *		48.5 "		
" <i>alba</i>			38.607 "	41.29 "
" <i>offinialis</i>				41.93 "
<i>Acanthus ilicifolius</i>			33.258 "	24.92 "
<i>Bruguiera gymnorhiza</i>		30.3 "	32.234 "	27.90 "
<i>Nesuvium Portulacastrum</i>			25.38 "	26.66 "

The other mangroves behave in a similar manner. However in the brackish water mangroves, the osmotic values are lower (under 24 atms.); and according to Walter, the results found here do not agree with those already recorded. Also the osmotic value of the shoots is considerably lower than that of other parts, such as roots, stems, etc, and even lower than that of the rind of the fruit; in fact it is lower than the osmotic value of the soil solution.

While studying the water storing capacity of the mangrove plants of East Africa, Walter (25) found that the concentration of the soil solution rises in the case of sea coast mangroves from outwards towards the interior. The concentration becomes considerably higher than that of sea water in the fourth zone *i.e.* *Avicennia* zone.

The soil of the mangrove forest even at low tide is always completely saturated with water. The transpiration activities are very low. The water content can thus be increased only through the presence of the osmotically active salts in the soil solution.

The water storing capacity of halophytes does not appear to be different from their salt capacity. Neither is it known in which proportion the halophytes gather water and salt from the

* *A. marina*, Vierh = *Scyura marina*, Forsk = *A. officinalis*, Linn.

(8) quoted in the introduction. Further this fact can be clearly seen when we compare rainfall and temperature (Fig. 5).

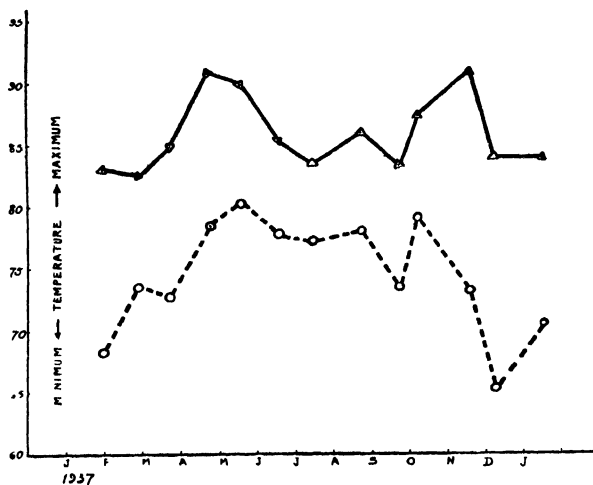


Fig. 5

Again it is remarkable to notice that throughout the year the graph of the osmotic pressure runs almost parallel to that of the actual maximum temperature of the day on which the samples were collected Table 6 (Fig. 5). Thus it shows that the osmotic pressure varies directly with the maximum temperature. Also it will be interesting to see from the graphs of the osmotic pressure (Fig. 3) and relative humidity Table 6 (Fig. 6) at the hour

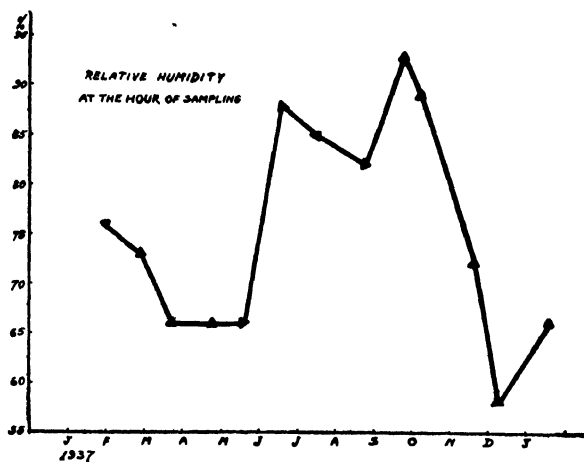


Fig. 6

of sampling, that the osmotic pressure of the leaf cell sap varies inversely with the relative humidity at the hour of sampling, that is to say when there is a rise in the relative humidity there is a corresponding fall in the osmotic pressure. This fact confirms the statement already made by Cooper and Pasha (9, 10). The sudden fall that we notice in the osmotic pressure in the month of September can be accounted for in the following way :—

- (1) As the maximum temperature of the day of sampling falls suddenly there is also a corresponding big rise in the relative humidity, which ultimately brings about the decrease in the osmotic pressure.
- (2) As the tide of the day fluctuated most on the day of sampling, reaching 3·2 feet at low tide and 15 feet at the high tide, the vegetation was exposed to the humidity for a larger surface, as well as immersed in the water for a longer time. The sampling was made at the low tide and owing to a greater surface exposed with at the same time increased humidity, naturally the osmotic pressure was lowered considerably.

CONCLUSIONS

The osmotic pressure of the mangrove leaf cell sap (*Avicennia alba* Bl.) varies—

1. directly with (a) the tide, (b) the temperature, and (c) the rainfall ; and
2. inversely with the humidity.

TABLE 6

Date	Time of Collecting the leaf samples	Relative humidity at the hour of sampling	Average rain fall (monthly)	Temperature		Tide		Height of sea water from the mean sea level at the hour of samp- ling (in feet)
				Max. °C. (During the day)	Min. °C. (During the day)	Maximum height in feet	Minimum height in feet	
27-2-37	8-15 A. M.	73	0.50"	82.5	73.5	14.15	2.95	3.90
22-3-37	3-10 P. M.	66		84.8	72.6	11.8	4.85	4.25
22-4-37	3-25 P. M.	66	0.01"	90.9	78.4	12.35	4.25	5.65
18-5-37	12-50 noon	66		89.7	80.3	11.4	5.16	5.8
18-6-37	12-55 noon	88	18.32"	85.4	77.7	10.8	5.85	8.2
15-7-37	2-50 P. M.	85	30.42"	88.5	77.2	11.15	5.65	10.2
23-8-37	8-7 A. M.	82	5.45"	86.0	78.6	14.35	2.05	4.4
32-9-37	8-15 A. M.	93	14.20"	83.2	73.2	14.9	1.7	4.2
7-10-37	7-49 A. M.	89	1.77"	87.2	79.0	13.45	3.25	5.2
19-11-37	7-47 A. M.	72		90.8	73.0	15.25	2.3	6.0
8-12-37	8-25 A. M.	58		83.8	65.1	12.6	4.7	6.2
18-1-39	9-30 A. M.	66		83.2	71.5	12.5	4.9	10.1

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BOTANICAL STUDY OF EXOTIC PINEAPPLE VARIETIES.

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Pineapple (*Ananas sativus*, Lindle) is one of the important commercial crops which has not yet been grown to any extent by the local growers in the Province of Bombay. There are, however, a few indigenous types in existence, the fruit of which is small, less juicy, fibrous and contains numerous seeds. But no attempt has been made to breed better types out of these forms. Only a few years ago, however, two exotic types of commercial importance were introduced with some success in this Province.

During the course of the writer's work on pineapple, these types came under his close observation and, therefore, a detailed botanical study was made which is presented below. In the available literature no reference is found regarding the botanical study of these varieties since their introduction in this country and hence this study.

The two exotic pineapple varieties introduced in the Province of Bombay are the Queen and the Kew (Smooth Cayenne).

The origin of these varieties is still obscure. As regards the Queen, the exact origin is not known and regarding that of the Kew (Smooth Cayenne), the available records give a rather confusing account. It was observed (Johnson, 1935) to be growing in the Royal Kitchen Gardens of Versailles some time in the year 1841 but the same authority states elsewhere that the planting material of the Kew pineapple was being imported from French Guinea.

The Queen and Kew varieties of pineapple were introduced in the Province of Bombay only about a decade back, their planting material having been obtained from Assam and Ceylon respectively.

The performance records of these varieties under field conditions show that their behaviour with regard to the size of fruit and the production of planting material have been consistent. The size and quality of fruit compare favourably with those

produced in other pineapple growing regions. It is, however, probable that these varieties might exhibit morphological variations under different ecological conditions but under conditions of soil and climate natural to their growth, the size and quality of fruit are unaffected.

THE QUEEN PINEAPPLE.

Stem :—Very short but robust. The plant bears clusters of leaves which spread out prominently from 4'·2" to 4'·5". Leaves are produced in whorls which vary in number from 18 to 21 in a medium sized plant and 30 to 40 in a fully developed plant. Leaves are linear with parallel venation, sessile, thick with serrate margins. Margins are armed with hard hooked spines. Apex acuminate terminating in a sharp point. Normally, the colour of the leaves is a light green. Leaves are 2'·3" to 2'·5" long and 1·4" broad.

Inflorescence :—Belongs to the class of indefinite or racemose type and is a spike. The fleshy axis and the numerous flowers fuse together to form a composite fruit called sorosis. The shape of the fleshy spike is globose or ellipsoid. Flowers on the axis are sessile. This variety produces flowers freely, producing on an average 116 flowers with a maximum of 155.

Flower :—Regular, hermaphrodite, epigynous, sessile and bracteate. Bract ovate having serrated margins. Apex acuminate gradually narrowing down to a fine acute point. It is 0·8" to 1·0" long and 0·2" to 0·4" broad. The two surfaces are finely pubescent with plenty of bloom. It is thick and fleshy to about half the length from the base. The bract is persistent.

Calyx :—Three, gamosepalous, ovate, fleshy. Colour greenish at the base and orange yellow to pale pink above. Sepals have a finely serrated margins and terminate in an acute apex which is slightly drawn out. Sepals 0·4" to 0·5" long and 0·3" broad. Sepals epigynous, superior. Upper surface pubescent with bloom. The under surface is greenish white, glabrous and devoid of bloom.

Corolla :—Three, regular, polypetalous. Petals 0·8" to 1·0" long and 0·2" to 0·3" broad, fleshy, white to about half the length and purple towards the top. Corolla cruciform with linear petals.

Stamens :—Six, but three out of the six are inserted opposite the petals and are apt to be mistaken for epipetalous stamens. The remaining three are inserted opposite to the

sepals. Epigynous, 0.6" long. Anthers dorsifixed, the type of dehiscence being introrse.

Pistil.—Tricarpellary, syncarpous with three distinct stigmas. Stigmatic region pubescent with plenty of secretion. Ovary trilocular with axile placentation, epigynous, inferior. Style 0.8" long. Ovules numerous, anatropus, unfertilised.

Fruit.—Cylindrical, 7.5" to 9.5" long having a girth varying from 1'-2" to 1'-5". Crown single and rarely multiple. The crown leaves are linear and serrated with hooked spines. The average width of crown leaves is 0.7".

The fleshy calyx during the process of development of fruit gradually gets depressed in such a way as to cause its margins to fuse together, thereby giving a uniform depressed area which is covered with plenty of bloom. The petals after drying twist round and assume dark brown colour and remain persistent. The dry and twisted corolla envelops the essential organs in dry condition. The average 'eye' width after the fruit is fully developed is 0.9". When the fruit is fully developed, the 'eyes' at the base flatten completely while those at the top remain undepressed.

When fully developed, the fruit is lightish green in colour but when ripe, it assumes a rich, deep yellow colour. The fruit on cutting shows the non-edible region of the 'eyes' followed by the edible flesh and lastly the core which is slightly tough and insipid in taste. The flesh is remarkably juicy, sweet, melting and devoid of fibre. Colour of the flesh is yellow. The length of the flesh and the diameter of the core vary from 1.3" to 1.6" and 0.6" to 0.8" respectively. The average weight of the fruit is three pounds, but fruits weighing five pounds are also not uncommon. The aroma is very pleasant and characteristic of the Queen pineapple. It is on account of this penetrating aroma that sometimes snakes are attracted to it and are seen to lodge just underneath the fruit without doing any damage.

Planting material.—The Queen pineapple produces suckers and slips or nibs freely often profusely, the averages being four and five respectively. It has been observed that 80 to 85% of the plants produce suckers before the appearance of the fruit. This variety, however, rarely gives out crown slips.

Slips are produced from the collar of the fruit down on the fruit stalk up to a length of 6.4". Slips are buds produced in the axils of young leaves and in the course of their development and emergence, they split the leaves at the base. The arrange-

ment of slips on the stalk is of two types; *viz.* (a) those that appear at the collar develop in cyclic order and (b) those appearing lower down, develop spirally.

THE KEW PINEAPPLE

Stem and Leaves :—Similar to that of the Queen. Leaves are produced in whorls which vary in number from nineteen in a medium sized plant to thirty or more in a fully developed plant. Leaves are curved, entire but the apical region is armed with hooked spines up to a length varying from 1.7" to 2.1". Leaves are 2'-7" to 2'-9" long and 2.2" to 2.4" broad. Leaves are green with a distinct brown strip along the centre extending the length of the leaf with green edges. The under surface is green with plenty of bloom. The bloom can be easily rubbed off exposing the green colour beneath. The young leaves are pinkish in colour to about half the length from the base; the margins being entirely serrated having conspicuous spines. When the leaves attain a large size, the spines disappear and the margins become entire.

Inflorescence :—Same as the Queen. This variety produces comparatively a small number of flowers and there appears to be quite a wide variation between the average and the maximum, giving 46 and 127 respectively.

It may be mentioned here that the number of flowers borne on the inflorescence in either the Queen or Kew is likely to vary considerably due to environmental factors of which nutrition is regarded as an important one.

Flowers :—Regular, hermaphrodite, epigynous, sessile, bracteate. The colour of the bract is green at the base and pink towards the top while the under surface is green at the base and reddish at the top. The under surface is finely pubescent. The two surfaces are covered profusely with bloom. The bract is thick and fleshy and is 0.9" to 1.0" long and 0.3" to 0.5" broad.

Calyx :—Three, gamosepalous, thick and fleshy, 0.4" long and 0.3" to 0.4" broad. The apex of the sepal is not so much drawn out as in the Queen. The other characters are similar to those of the Queen.

Corolla :—Three, regular, polypetalous. Petals are fleshy, white to about half the length and lilac at the top, linear, 0.8" to 0.9" long and 0.2" to 0.3" broad. Each petal has on its under surface at the base two fleshy appendages on either side of the margin touching each other in such a way as to form a groove in which one stamen is snugly held in position. Petals persistent.

Stamens :—Same as in the Queen with the exception that of the six stamens, three lie in between the two appendages at the base of the corolla while the remaining develop freely in between the petals. Stamens 0.6" long.

Pistil :—Tricarpellary, syncarpous with three short stigmas. Style 0.7" long. Ovary trilocular with axile placentation, epigynous, inferior. Ovules numerous but unfertilised.

Fruit :—Fruit cylindrical 9" to 11" long having a girth varying from 1'4" to 1'8". A large size fruit has a tendency to taper towards the apex while the small size fruit is nearly cylindrical. The average weight of the fruit is eight pounds although fruits weighing twelve to fourteen pounds are not uncommon. The 'eyes' which are brown and flat are deep purple in colour and are larger than those of the Queen having a width of 1.3". Crown multiple. Crown leaves linear, entire but sparsely serrated to an average length of 0.4" from the apex. The width of the leaves is 1.8".

The fruit on ripening assumes a light orange-yellow colour, juicy, sweet-acid in taste and slightly fibrous. It lacks aroma which is so much pronounced in the Queen. The average length of flesh and the diameter of the core are 2.1" and 0.8" respectively. The flesh is light yellow in colour with localised areas of white tissues.

Planting Materials :—Kew pineapple is a shy bearer of suckers and more so of slips which average two and nil respectively. It, however, produces crown slips liberally giving an average of five per plant. The noteworthy feature of this variety is that unlike the Queen, it does not produce suckers before the appearance of the fruit.

The Queen and Kew varieties of pineapple exhibit a few common features in regard to the following important characters :—

- (a) character of the crown,
- (b) opening of flowers,
- (c) arrangement of flowers, and
- (d) period of the opening of buds.

(a) *Character of the Crown* :—

Plants of either variety exhibit different types of crown and crown leaves *viz.* (1) when the crown is short and compact, the crown leaves are short and (2) when the crown is loose and elongated, the leaves are comparatively longer.

(b) Opening of Flowers:—

The fully developed flower buds commence to open some time at mid-night and take nearly three hours for complete opening if the weather is warm and still. If the opening is immediately followed by dew fall or it occurs when they are just about to open, it takes nearly four hours for complete opening. It is observed that the factors which delay full blooming are dew, cold winds, cloudy weather and rain.

(c) Arrangement of Flowers:—

The order of opening of flowers on the rachis is from bottom upwards. The arrangement of flowers on the rachis is in a cyclic order. The number of flower whorls varies widely in fruits of the same variety depending upon the size of the fruit.

(d) Period of the Opening of Buds:—

The analysis of the period of anthesis shows that in the case of the Queen, it takes 2-3 days for complete opening from the time the buds appear. In the case of the Kew, however, the period of anthesis is 4-5 days.

SUMMARY

The chief distinguishing features of the Queen and Kew varieties of pineapple whose botanical characters are explained at some length in the foregoing pages, are summarised as follows:—

The conspicuous feature of the Queen pineapple is that the leaf margin is armed with hooked spines while that of the Kew, it is entire. The leaf colours of the Queen and Kew are markedly different, being reddish brown with greenish base and a distinct brown centre along the length of the leaf with green edges respectively.

Unlike the Queen, the flower mechanism of the Kew is peculiarly characteristic. Each petal shows two fleshy appendages on either side of the margin forming a groove in which a stamen is snugly held in position.

There is a marked difference in the size of the fruit as regards girth and weight, being 1'-5" and 3 lbs. respectively in the Queen and 1'-8" and 8 lbs. respectively in the Kew. Although the average weight of the Kew is 8 lbs., fruits weighing 12 to 14 lbs. are not uncommon. The 'eyes' in the Queen are smaller and light green in colour while those of the Kew are larger and deep purple in colour.

The fruit of the Queen pineapple, assumes on ripening, deep yellow colour and the flesh which is yellowish in colour,

is abundantly juicy, sweet and free from fibre. It possesses a characteristic aroma which is pleasant and penetrating. The fruit of the Kew, on the other hand, assumes after ripening, light orange colour. The flesh which is of pale yellow colour, is juicy, sweet-acid in taste and slightly fibrous. It lacks aroma which is so pronounced in the Queen.

The other marked differentiating feature of these varieties is in their nature of production of planting material. Unlike the Queen which produces suckers and slips freely, the Kew pineapple exhibits a peculiarly shy tendency in this respect. It, however, produces crown slips profusely. The production of crown slips is practically absent in the Queen except in rare cases. Another contrasting feature of these two varieties is that the Kew ordinarily does not give out suckers before the appearance of fruit but a large majority of Queen plants produces suckers before the fruit emerges. The extent to which planting materials are produced in the Queen and Kew varieties of pineapple is as follows:—

Variety		Suckers	Slips	Crown slips.
Queen	...	4	5	...
Kew	...	2	...	5

The points of similarity exhibited by these varieties are those of the time of anthesis and the period of the opening of buds. The opening of flowers is observed to commence late at night and takes nearly three hours, depending upon weather conditions. The period of anthesis is influenced by dew, cold winds, cloudy weather and rain. It takes 2-3 days and 4-5 days respectively for flower buds of the Queen and Kew for complete opening from the time the buds appear.

ACKNOWLEDGEMENT.

The helpful interest of Dr. G. S. Cheema, Horticulturist to Government, Province of Bombay, Poona, at whose suggestion this work was begun and of Professor L. S. S. Kumar, Economic Botanist to Government, Province of Bombay, Poona, is gratefully acknowledged.

Literature Cited.

1. Johnson, M. O.—1935, The Pineapple, page 283.

ALGAE OF THE MALWAN HARBOUR

By

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The marine algae of the northern part of the coast of the Bombay Presidency are fairly known to us through a series of papers published by Boergesen¹ in India and abroad. However, very little information is available regarding the algal forms of the southern shores of the Bombay province. The littoral flora of Ceylon is also known to a certain extent but the very rich coast-line between Ceylon and Bombay remains to be explored by the scientists. So far as the writer is aware there is only one paper² on a few algal forms of this intermediate region. The existence of Australian, Japanese and the Northern Atlantic species as pointed out by Boergesen, as far north as Karachi in the Arabian Sea, adds great plant-geographical interest to this exploration of the south-west coast. It is also shown that the algal vegetation at Bombay differs from that of the North. The phanerogamic land flora of the Bombay province has two distinct types, *viz.*, the Arabio-African in the North and the Indo-Malayan in the South. Therefore, it would be quite interesting to ascertain if the marine flora of the province has some such parallel divisions.

The author had an opportunity of visiting Malwan* for a week in the middle of March 1928. Malwan has a beautiful

1. Boergesen, F. :—A list of Marine Algae from Bombay :—

Det Kgl. Danske Videnskabernes Selskab. Biologiske Meddelelser XII, 2. Kobenhavn, 1935.

:—Some Marine Algae from the Northern part of the Arabian Sea with remarks on their geographical distribution. *Ibid.* XI, 6. 1934.

:—Some Marine Algae from Ceylon. The Ceylon Journal of Science Section A. Bot. Vol. XII, part 2, Oct. 1936.

2. Barton, Ethel:—List of Marine Algae collected at the Maldive and Laccadiv Islands by J. S. Gardiner. Linn. Soc. Bot. Vol. 35 (1903), pp. 475-82, 13 pl.

* Malwan is a small coastal harbour one hundred and eighty-five miles south of Bombay in latitude 16°3'N. and longitude 73°30'E.

long sandy beach fringed by a rich phanerogamic vegetation in between Coconut and Casurina plantations. There, the great quantities of sea-weeds thrown out by the sea are collected by the people and used as green manure for the coconut trees. Most of the rocky portion of the harbour is near the fort and to the north of the town. The algal vegetation in March, when the cold weather nearly ends, could not be said to be luxuriant and it appeared as if the large part of it had almost died down. Out of a very small collection of plants made during that brief visit a small paper¹ was published in this journal in 1933. In that paper the writer has recorded seven species of *Caulerpa*. One of them *viz* *Caulerpa verticillata* J. Ag. is so far known to occur round about Ceylon in the Indian ocean. The present paper records the remaining thirty plants. Some additional species of *Laurencia*, *Chondria*, *Acanthophora* and *Gelidium* could not be identified owing to the material either being scanty or sterile. However, the few plants recorded here show the extension of some of the species at present only found at Bombay. It may also be mentioned that a search made for the species of *Udotea*, *Halimeda* and *Acetabularia* which occur on the coast of Kathiawar but not at Bombay was of no avail and not a single specimen of any of them was secured at Malwan. The geological formation at Malwan is basaltic like that of Bombay and unlike that of Kathiawar which is mainly a limestone one. The rainfall and the climatic variations are very much the same as at Bombay.

The plants were preserved in 4 p. c. solution of formalin in filtered sea-water for the microscopic study.

The author wishes to express his grateful thanks to Dr. F. Boergesen of Copenhagen for the determination of some specimens sent to him.

SYSTEMATIC ENUMERATION OF THE SPECIES OBSERVED

Class Chlorophyceae

ORDER Ulotrichales

Family Ulvaceae

Genus *Enteromorpha* Link.

1. Dixit, S. C:—Caulerpaeae from Malwan Harbour. *Jour. Univ-Bom.* Vol. I, 5, 1933, p. 35.

1. *Enteromorpha flexuosa* (Wulf.) J. Ag. Boergesen, "Some Marine Algae from the Northern part of the Arabian Sea." Biologiske Meddeleser VI, 6, Kobenhavn, 1934, p. 6.

Fronds tubular, simple or occasionally branched at the base, 2-15 cm. long, 5-9 mm. in diameter, slightly contorted above and inflated like those of *E. intestinalis* Link. Surface cells roundish polygonal, 10-18 μ broad, arranged in irregular longitudinal rows.

Habitat :—On rocks, stones, shells and on old boats.

Genus *Ulva* Linn.

2. *Ulva Lectuca* (L.) Le Jolis, "Algae marines de Cherbourg," 1863, p. 38. Setchell and Gardner, Chlorophyceae, Mar. Alg. of Pacific Coast of N. America, p. 265.

Frond leaf-like, two cell-layers thick, about 60 μ thick in cross-section, firm in texture, ovate in shape, short stipe at the base, fixed by disc-like hold-fast, 5-30 cm. long, often perforated. Surface cells 2-4 together, cells 20 μ long, 10 μ broad.

Habitat :—Larger forms abundant in the rock-pools of the upper limits of the tidal zone; smaller forms on open and sheltered rocks. These plants were luxuriously growing near the Oyster beds and creeks. The smaller forms were much crumpled and varied in colour from dark green to yellowish green and completely bleached when old.

ORDER Siphonocladiales

Family Boodleaceae

Genus *Cladophoropsis* Boergs.

3. *Cladophoropsis Zollingeri* (Kütz.) Boergs. Boergesen, Jour. Ind. Bot. Soc., Vol. XII, No. 1, 1933, p. 2, Fig. 1.

Plants 2cm. high, forming puff-like intricate mass 2-3 cm. broad. Ramification opposite below but mostly unilateral above. The cross-walls in the branchlets are generally not formed on the apical parts and when formed not quite at the base. Crass. fl. 80-160 μ . Plants fixed by rhizoids and tenacula. In some of the upper cells green ball-like cell-contents are present.

Habitat :—On sand covered rocks; in habit very much like and in association with *Rhizoclonium grande* Boergs.

The plant is very much like *Cladophoropsis sundanensis* Reinbold as the writer has seen specimens of both the species

from Bombay and finds that the differences are difficult to make out.

Family Cladophoraceae

Genus Chaetomorpha Kütz.

4. *Chaetomorpha media* (Ag.) Kütz. Boergesen, Jour. Ind. Bot. Soc., Vol. XI, 1932, p. 51. Boergesen, Marine Algae from the Canary Islands, Chlorophyceae, Copenhagen, 1925, p. 37.

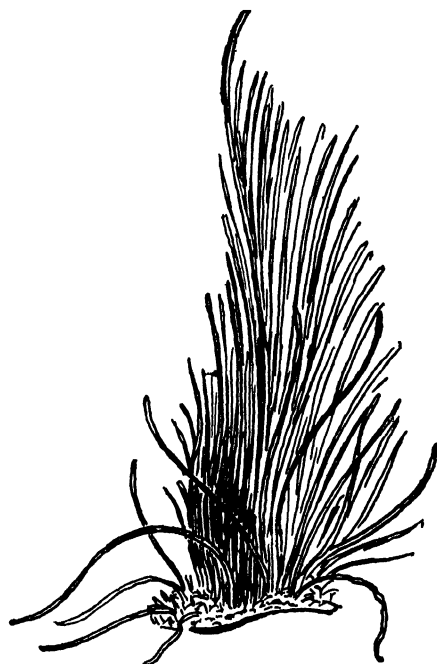


FIG. 1. *Chaetomorpha media* (Ag.) Kütz. Tuft showing the habit of the plant. (1:1)

Plants forming brush-like tufts; filaments 5-7 cm. long, having on the average about 100 cells; longer cells towards the base, the shorter ones near the apex. The basal cell is the longest one, as much as 12 mm. before the first transverse wall appears. Some filaments have annular constrictions at the base. Lat. cell., 125-175 μ . basal cell; 300-350 μ . apical cell; long. cell., 400-800-1500 μ . Lamellose cell-wall 25-80 μ . thick. The tips of the larger filaments have white empty cells and lateral pores in the cell-walls indicating the escape of the zoospores.

The rhizoids of the numerous filaments of the tufts form an inseparable interwoven disc at the base. The rhizoids show many papillose swellings which appear to be developing into new filaments. The rhizoids are non-septate and stained with iodine reveal no starch but condensed dark green protoplasmic contents.

Habitat :—On open and mostly submerged rocks.

Ulvea lens Crouan (Chaetophoraceae) were epiphytic on these plants, forming discs upto 150–200 μ in diameter.

Genus *Rhizoclonium* Kutz.

5. *Rhizoclonium grande* Boergs. Boergesen, A list of Marine Algae from Bombay, Biologiske Meddelelser, XII, 2, Kobenhavn, 1935, p. 14, Figs. 5–6.

Plants form intricate roundish clumps; filaments irregularly curved, 8 cm. or more long. Lat. cell., 320–365 μ ; long. cell., 415–665 μ ; crass. cell-wall 35–83 μ , lamellose. Rhizoids scarce, non-septate. Akinets present in some filaments.

Habitat :—On rocks near low-water mark.

The Malwan plants differ from the Bombay specimens by the greater length of the filaments and the scarcity of rhizoids, otherwise they are almost similar. The cell-wall shows little reaction by sulphuric acid and iodine.

Family Anadyomenaceae

Genus *Valoniopsis* Boergs.

6. *Valoniopsis pachynema* (Martens) Boergs. Boergesen, Some Marine Algae from the Northern Part of the Arabian Sea etc. *Op. Cit.*, 1934, p. 13, Figs. 1–2.

Thallus cespitose, 6–10 cm. long, 500–650 μ in diameter. Chlorophyll parietal; walls of the coenocytic thallus membranous and tough. Thallus fixed by small blackish or brownish pad-like thickenings of the walls at about 0.5–1.5 cm. intervals. Branches mostly 2–3, rarely even 8, generally opposite. Primary and secondary ramification similar. Occasionally a branch is modified in a tendril like fashion with a curved tip. Branches clearly septate. The creeping thallus gives rise to the vertical branches 3–4 cm. high which intertwine and form cespitose body.

Habitat :—On rocks below low-water mark.

The plants resemble in all respects the Karachi specimens described by Boergesen but lack the vigorous hepters mentioned by him and are slightly smaller in dimensions. The pad-like thickenings of the walls of the thallus appear to be the modification due to their growth on hard impenetrable rocks.

Family Siphonocladaceae

Genus *Struvea* Sond.

7. *Struvea delicatula* Kütz. Murray and Boodle, A structural and systematic account of the genus *Struvea*. Ann. Bot., Vol. 11, p. 265.

Plants forming small tufts, 1-1.5 cm. high; 2-4 mm. broad; crass. stipe., 300-330 μ ; ultimate ramuli 100 μ broad. The expanded vertical primary or secondary shoots spring from a prostrate, irregular, profusely ramified rhizome like thallus at the base. Tenacula vigorously developed on the lateral branches. The cross-walls are first formed in the main stipe and the septations in the lateral branches follow later. Primary branches opposite. In older parts the cell-wall is lamellose, 30-50 μ thick.

Habitat :—On exposed rocks near the low-water mark.

This species is not the same as *Struvea anastomosans* (Harv.) Piccone or *Struvea ramosa* Dickie as it is smaller in size and has thicker cell-walls. But it certainly resembles them in its mode of growth. Compared with the specimens found at Bombay the Malwan plants are decidedly smaller in size.

ORDER Siphonales

Family Bryopsidaceae

Genus *Bryopsis* Lamour.

8. *Bryopsis pennata* Lamouruz. var. *secunda* (Harv.) Collins & Harvey. Taylor, "The Marine Algae of Florida," Carnegie Inst., Washington, 1928, p. 93, pl. 11, Fig. 12.

Plants simple, 4 cm. long; 2-3 simple pinnate fronds growing out from the same rhizoid. 1/8 of the lower part of the main thallus is naked but near the rhizoid there are 8-10 pinnule-like branchlets. The pinnules in the present plant are arranged on one side of the frond above the naked 200-330 μ broad stalk like portion of the frond. Pinnae cylindrical 70-100 μ broad, upto 2 mm. long, incurved, obtuse, swollen at the tips,

constricted at the base. Branches infrequent and the plant shows metallic iridescence.

Habitat :—On corals and shells in deep water.

This plant according to Bergesen would be a variety of *B. plumosa* Ag. but looking to the very different nature of pinnules, their origin and the simple nature of the plant it should be regarded as a distinct species. *B. plumosa* Ag. found at Karachi is a very large, compound plant and its pinnules have very definite arrangement. The Malwan plant agrees completely with the plant from Florida.

Family Codiaceae

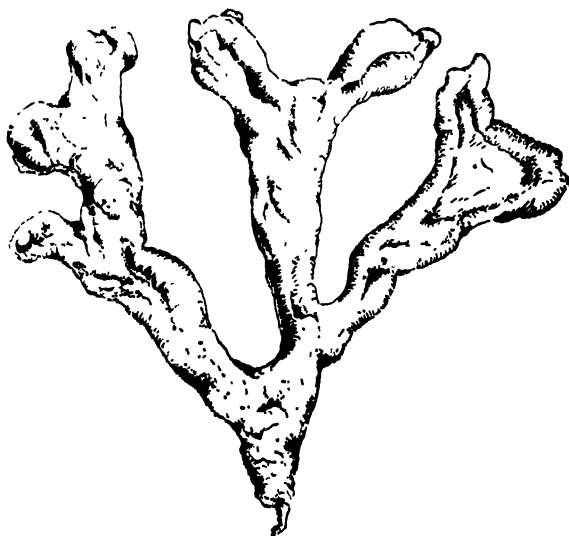
Sub-family Codieae

Section Elongata De Toni.

Genus *Codium* Stackh.

9. *Codium indicum* sp. nov.

This very robust, light green and large plant is unlike any of the species described so far. Frond 20-25 cm. long,

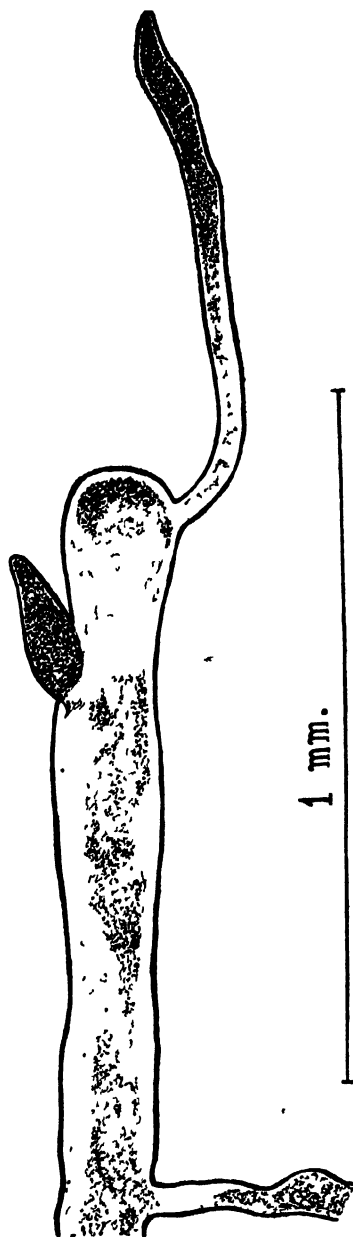


(a)

FIG. 2. *Codium indicum* sp. nov. (a) Part of a thallus, $\frac{1}{2}$ the Nat. size.

(b) Small vesicle with gametangium.

2.5-3.2 cm. broad, irregularly flattened; dichotomously branched at 3-7 cm. distance between the branching. The thallus below



(b)

the ramification is broadly cuneate ; tips bluntly lobed. Vesicles

352 μ broad, 1120 μ long ; gametangia 80 μ broad, 192 μ long. Vesicles vary in form from ovate fusiform to narrowly fusiform. Hair-like outgrowth often present, gametangia 1-2.

Habitat :—In deep waters ; mostly cast ashore at high tide.

This new species is extremely robust and larger than any as yet recorded and differs in the form of its branching, apices, size of the gametangia and the general make-up of the plant. The author has seen two other kinds of specimens from Dwarka and Karachi. From Dwarka, the specimen recorded as *Codium elongatum* Ag. by Boergesen in the Journal of the Indian Botanical society, vol. IX, No. 2-3, 1930, pp. 159-60 is quite unlike the one from Malwan. It also differs from *Codium elongatum* Ag. described by the same author in "Marine Algae from the Canary Islands," I, Chlorophyceae, 1925, pp. 94-97, in the ramification and the shape. The Dwarka specimen has no cuneate enlargement of the thallus below the furcation. It is also olive-green and cylindrical and not at all flattened. In March 1938 specimens of *Codium* were collected at Manora-Karachi and the author noticed that two different kinds of specimens were growing side by side in the littoral belt. One of them was exactly like the Dwarka specimen but the other one had rather a flattened and cuneate thallus under the furcations. Hence it is thought that both the forms belong to the different species.

It also appears that *Codium elongatum* Ag. is taken as *Codium decorticans* (Woodw.) Howe. If the Malwan plant resembles at all any other species it is with the *Codium decorticans* which is a much larger plant. But the description of that species is so vague that there is no certainty about its identity. It is, therefore, preferred here to give this Malwan plant a specific name of its own so that the confusion may not become worse confounded. In this connection attention may be drawn to the remarks made by Setchell and Gardner on these species in the Univ. of California publications on Botany, Vol. 8, No. 2, 1920, pp. 172-174.

Lyngbya infixa Frey (Frey, Les Cyanophycees des Cotes d'Europe in Memoires de la Societe Nationale des Sciences Naturelles et Mathematiques de Cherbourg, t, XLI, Saint-Lo, 1934, p. 110) grew on the apices of the Malwan plant.

Class Phaeophyceae

ORDER Ectocarpales

Genus *Rosenvingea* Boergs.

10. *Rosenvingea orientalis* (J. Ag.) Boergs. Weber van Rosse, A. Algas du Siboga, I, 1913, p. 137. Boergesen, Journ. Ind. Bot. Soc., Vol. IX, p. 168, 1930.

The thallus forms a hollow, tubiform filament 2-4 mm. broad, 6-8 cm. long; often with many blunt proliferations. The inner cells of the thallus are elongated. The specimens had superficial plurilocular sporangia formed in clusters. Hairs were only present on mature filaments.

Habitat:—On Rocks below low-water mark; cast ashore by tide.

The breadth of the tubiform filaments "1 cm. to about 5 cm." mentioned in Dr. Boergesen's paper cited above appears to be a misprint.

Family Encoeliaceae

Genus *Colpomenia* Derb. et Sol.

11. *Colpomenia sinuosa* (Roth.) Derb. et Sol. Hauck, Die Meersalgen, Deutschlands und Oesterreich, Leipzig, 1885, p. 393, Fig. 171. Boergesen, Mar. Alg. D. W. I., p. 176, Fig. 138.

Thallus brown, rounded, hollow, sometimes crumpled, 4-7 cm. diam. Internal cells of the thallus large, colourless; outer cells small, packed with chromatophores. Hairs in tufts, scattered. Plurilocular sporangia with paraphysis not developed.

Habitat:—On mud and roots of mangroves, fixed by fine, branched rhizoids.

There are two distinct forms of this plant; one form is small ball-like and bulbous, the other form is large, crumpled and lobed.

ORDER Sphacelariales

Family Sphacelariaceae

Genus *Sphacelaria* Lyngb.

12. *Sphacelaria furcigera* Kütz. Oltmanns, Morphologie U. Biologie Der Algen, Band II, 1922, p. 94, Figs. 3-5. Newton, British Sea-weeds, London, 1931, p. 189.

Plants in small tufts, 1 cm. high, poorly branched at the base. Diam. fil. 33-36 μ . Propagula slender, with two rays; stalk of propagula 250-400 μ long, 16-24 μ diam., arms slender, 180-200 μ long. Unilocular sporangia ovoid above, cylindrical below, 45-48 μ long 15-17 μ broad, on unicellular pedicel.

Habitat :—Epiphytic on larger Phaeophyceae; it fixes its rhizoids into the thallus of the host plant.

ORDER Dictyotales

Family Dictyotaceæ

Genus *Spathoglossum* Kütz.

13. *Spathoglossum asperum* J. Ag. Boergesen, *Op. Cit.*, 1935, p. 35, Pl. V.

Fronds dark-brown, 20-35 cm. long, sub-dichotomously divided, final ramification unequal, lower parts more or less dentate. Fructifications scattered all over the surface of the thallus; specimens tetrasporangiate.

Habitat :—on the rocks below the low-water mark.

Genus *Stæchospermum* Kütz.

14. *Stæchospermum marginatum* (Ag.) Kütz. Boergesen, Jour. Ind. Bot. Soc., Vol. XI, 1932, p. 67, Fig. 8.

Fronds 7-15 cm. long, 0.5-1 cm. broad; spatulate proliferations at the base; apices unequal; hold-fast button-like; tip of the thallus in-rolled; groups of hairs on the thallus present; tetrasporangia marginal.

Habitat :—In rock-pools about the low-water mark.

Genus *Padina* Adans.

15. *Padina tetrastromatica* Hauck. Weber van Bosse, *op. cit.*, 1913, p. 180 Boergesen, Jour. Ind. Bot. Soc., Vol. IX, 1930, p. 172, Fig. 10, Pl. II.

Plant yellowish dark brown, 8-12 cm. high, fan shaped and simple when young, old fronds divided into irregular lobes, 1-2 cm. broad. Upper margin in-rolled. Thallus with layers of cells 2-4, colour bearing rectangular cells on either side of central elongated cells. Hairs usually well-developed near the basal portion. Tetrasporangia along each side of a row of hairs

in concentric zones, 50–80 μ diam. Tetrasporangia maturing from the lower parts upwards.

Habitat :—On rocks or stones but under water.

Genus *Dictyopteris* Lamour.

16. *Dictyopteris Woodwardii* (Brown.) J. Ag. Boergesen, South Ind. Mar. Flora, II, Jour. Ind. Bot. Soc., Vol. XVI, 6, 1937, p. 316.

Fronds tufted, 20–30 cm. high, $\frac{3}{4}$ –1 cm. wide, linear, dichotomously divided, midrib conspicuous, lamina often torn; margin dentate; tetrasporangia on either side of the thallus near the midrib. The plants emit pungent smell when fresh. Hold fast discoid.

Habitat :—On rocks at great depths; mostly cast ashore.

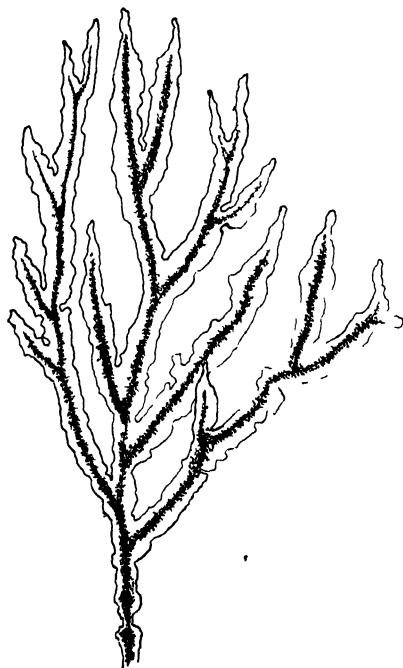


FIG. 3. *Dictyopteris Woodwardii* (Brown.) J. Ag. Showing torn lamina. $\frac{1}{2}$ the Nat. size.

Genus *Dictyota* Lamour.

17. *Dictyota Bartayresiana* Lamour. Taylor, *op. cit.*, 1928, p. 117, Pl. 16, Fig. 16, Pl. 19, Fig. 10.

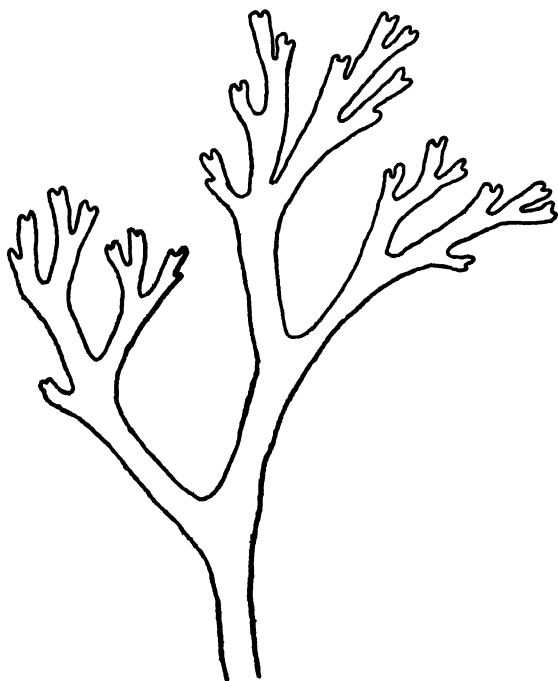


FIG. 4. *Dictyota Bartayresiana* Lamour (1:1)

Frond thin, sticky light brown, 10-12 cm. high, 2-5 mm. wide, distance between dichotomy 1-2.5 cm.; tips slightly unequal. Thallus parenchymatous with a single middle layer bounded by a surface layer on each side. Fructifications well developed on the lower portions and near the margins. Tetrasporangia scattered, 90-130 μ diam.

Habitat:—On rocks below the low-water mark; cast ashore.

18. *Dictyota dumosa* Boergs. Boergesen, *op. cit.*, 1935, p. 37, Pl. VI.

Plants dark brown, tufted, 12-20 cm. high, dichotomously branched, forming ribbons 0.5-1 cm. wide; ultimate branches broadly forked; apices obtuse; distance between dichotomies 2-4 cm. Tetrasporangia 95-105 μ diam., irregularly developed.

Habitat :—In rock-pools about the low-water mark.

ORDER Fucales

Family Fucaceæ

Genus *Sargassum* Ag.

19. *Sargassum cinereum* J. Ag. var. *barberifolia* Grun. Boergesen, Jour. Ind. Bot. Soc., Vol. XII, 1933, p. 13, Fig. 7, Pl. III.

Plants brown, stipe smooth, leaves alternate, 2-3½ cm. long, ½-cm. broad, apex obtuse, base wedge shaped, margin toothed; cryptostomes present; vesicles spherical, 3-6 mm. long, 2-4 mm. broad, with mucronate tip. Male and female receptacles in small panicles.

Habitat :—On rocks below low-water mark.

20. *Sargassum plagiophyllum* (Mert.) J. Ag., Boergesen, *op. cit.*, 1933, p. 15, Pl. V.

Plants brown, stipe smooth, round, 2 mm. thick; leaves linear oblong, 2-3 cm. long, ½-¾ cm. broad; margin entire or wavy; apex obtuse; base acute; cryptostomes scattered; vesicles small, spherical, 2 mm. broad, mucronate; receptacles branched.

Habitat :—In deep waters; cast ashore.

Class Rhodophyceæ

ORDER Gelidiales

Family Gelidiaceæ

Genus *Gelidium* Lamour.

21. *Gelidium corneum* (Huds.) Lamour. Taylor, *op. cit.*, 1928, p. 142, Pl. 28, Fig. 2. Boergesen. Mar. Alg. D. W. I. 4, p. 114, Fig. 124.

Frond red, cartilaginous, compressed, dichotomous, 3-4 cm. high, 2-3 pinnately branched or unbranched; branches 0.5-2 mm. broad, narrow at the base, apex rounded; tetrasporangia scattered in the cortex; branches with the cystocarps swollen with an ostiole on each side of the thallus.

Habitat :—On rocks in pools on the upper littoral belt.

ORDER Cryptonemiales

Family Squamariaceæ

Genus *Hildenbrandia* Nardo.

22. *Hildenbrandia prototypus* Nardo. Newton, *op. cit.*, 1931, p. 297, Fig. 184.

Thallus calcareous, encrusting in purple-pinkish patches on rocks and stones. Vertical cells 5-6 μ broad; upper and lower cells of the thallus vary in size. Tetrasporangia 20-25 μ long, 10-15 μ broad, pyriform, irregularly divided.

Habitat:—On exposed rocks and stones in the littoral zone above low-water mark.

Family Corallinaceae

Genus *Amphiroa* Lamour.

23. *Amphiroa fragilissima* (L.) Lamour. Weber van Bosse and M. Foslie, The Corallinaceae of the Siboga Expedition, LXI, p. 89, 1904, Pl. XVI, Figs. 1, 2, 5. Boergesen, Kew Bulletin, 1934, No. 1, p. 7.

Fronds tufted, reddish violet, articulated, cylindrical, twice or thrice forked at the nodes; joints long and swollen at the top and at the base. The central strand consists of 4-8 rows of elongated cells 70-100 μ long and 1-2 rows of short cells 20-25 μ long. Tetrasporangia 42-48 μ long, 20-24 μ broad. Conceptacles, round, prominent on the frond.

Habitat:—In rock-pools in the upper littoral zone. Plants become brittle due to excessive lime-encrustation.

24. *Jania rubens* (L.) Lamour. Hauck, *op. cit.*, 1885, p. 278. (*corallina rubens* L.) Newton, *op. cit.*, 1931, p. 314.

Fronds tufted, purplish red, 2-4 cm. high, dichotomously branched, cylindrical, segments 150-200 μ diam. Specimens sterile.

Habitat:—In rock-pools in the upper littoral zone.

Family Grateloupiaceae

Genus *Grateloupia*.

25. *Grateloupia flicina* (Wulf.) Ag. Boergesen, *op. cit.*, 1935, p. 53, Pl. VII-IX.; Newton, *op. cit.*, 1931, p. 273.

Fronds dark violet or blackish green, tufted, 6-14 cm. long, $\frac{1}{4}$ - $\frac{1}{2}$ cm. broad; pinnately branched, branches developed irregularly opposite or alternate on the main thallus. Tetrasporangia scattered over the thallus, cruciate.

Habitat:—On rocks in the tidal zone near the low-water mark. This species has extremely variable forms.

Genus *Halymenia* (Ag.) J. Ag.

26. *Halymenia dilatata* Zanard. Boergesen, Jour. Ind. Bot. Soc., Vol. XVII, No. 4, 1938, p. 214.

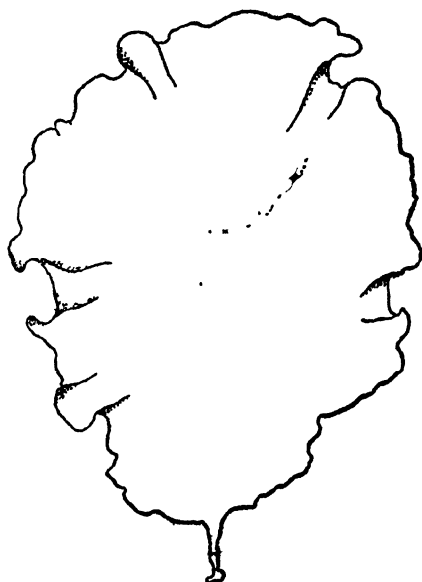


FIG. 5. *Halymenia dilatata* Zanard. Female specimen about $\frac{1}{2}$ the Nat. size.

Thallus rosy, flat, membranous, orbicular, tough, gelatinous, 30–45 cm. diam.; stipe 1–1.2 cm. long; margin denticulate; thallus often perforated; attached by a discoid holdfast. Tetrasporangia scattered over the thallus. Specimens female with cystocarps.

Habitat :—In deep waters; cast ashore.

ORDER Gigertinales

Family Hypneaceae

Genus *Hypnea* Lamour.

27. *Hypnea Valentiae* (Turn.) Mont. Boergesen, Kew Bulletin, 1934, p. 17.

Fronds filamentous, densely branched, greenish purple; branches short, crowded.

Habitat:—Cast ashore in tangled masses. The species is highly variable.

ORDER Ceramiales

Family Ceramiaceae

Genus *Centroceras* Kütz.

28. *Centroceras clavulatum* (Ag.) Mont. Taylor, *op. cit.*, 1928, p. 189, Pl. 28, Figs. 6-7. Oltmann, *op. cit.*, p. 295, Fig. 512 (1).

Plants filiform, forming entangled masses, dark purple, 4-6 cm. high; diam. fl. 116-165 μ ; spines mostly two celled; tetraspores sub-lateral, protected by spines.

Habitat:—On rocks above low-water mark.

Genus *Spyridia* Harv.

29. *Spyridia filamentosa* (Wulf.) Harv. Taylor, *op. cit.*, 1928, p. 197, Pl. 28, Figs. 4, 18. Boergesen, Mar. Alg. D. W. I., II, 233, Figs. 222-226. Newton, *op. cit.*, 1931, p. 394, Fig. 236.

Frond cylindrical, reddish, tough, 8-15 cm. high, corticate, branches many, irregularly placed, progressively thinning towards the tip. Branches beset with short, variable, ecorticate, occasionally ramuli curved, 450-800 μ long, 30-35 μ thick. Cystocarp stalked, situated on branchlets and surrounded by ramuli. Tetrasporangia spherical, sessile, on ultimate branchlets.

Habitat:—On rocks and stones near low-water mark, fastened by a discoid holdfast.

Family Delesseriaceae

Genus *Caloglossa* J. Ag.

30. *Caloglossa Leprieurii* (Mont.) J. Ag. Taylor, *op. cit.*, 1928, p. 161. Boergesen, Mar. Alg. D. W. I. II, p. 341, Figs. 338-339.

Plants small, greenish violet. Thallus flat, leafy, oval lobed, consisting of a single layer of cells except in the midrib portion, repeatedly forked and producing rhizoids at every furcation. Tetrasporangia rounded formed irregularly in the thallus.

Habitat:—On rocks upto high-water mark; on oyster beds and even in polluted water. This plant withstands considerable exposure.

A NOTE ON SOME ABNORMALITIES IN PLANTS COLLECTED IN BOMBAY—III

By

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*Supernumerary Leaflet of Crataeva religiosa, Forst ;
N. O. Capparidaceae*

The specimen described here was collected from the Botanical garden of the Royal Institute of Science in the year 1937, and since then the plant was kept under observation. It was noticed that every year during the monsoon, the plant bore approximately five to six such abnormal leaves, having a supernumerary leaflet interpolated above the normal three leaflets. Normally the plant bears trifoliate compound leaves (3), (Plate 1, fig. 1, a), which are disposed horizontally, at right angles to the incident rays. All the normal characters regarding the shape, size and position of the leaves were present in the specimens collected, except that a fourth leaflet (Plate 1, fig. 1, b and c), smaller than the other three was present. This fourth leaflet pointed vertically upwards, parallel to the incident rays. It grew from the same point from which the other three leaflets arose. It was about one-third to one-fourth the size of the normal leaflet, and in one or two cases, it was even bilobed (Plate 1, fig 1, b). This anomaly of an extra leaflet comes under the term "pleiophylly", which designates the appearance of two or more leaves in the place usually occupied by a single one. The term is also used for those normally compound leaves in which the number of leaflets is greater than usual. The term "pleiophylly" must not be confused with the term "polyphylly" which is used to designate the increased number of leaves in a whorl, as is often found in *Lonicera brachypoda*, *Weigela rosea*, *Vinca minor* etc. which normally have opposite leaves, but occasionally produce them in whorls of three (6). Pleiophylly in simple leaves has been reported in *Ulmus campestris*, *L.*, *U. montana*, *With.*, *Corylus*, *Mulberry*, (13), *Pomaderris elliptica*, (8), etc. and in the compound leaves of *Trifolium repens* (6) and *Cytisus Laburnum*, etc. (11). In all these cases the new leaflet arises either from the apex or from the base of the petiole. In the latter case it appears as if two leaves arose from the stem side by side.

Biswas (1) has described a leaf arising from the simple leaf of *Carica Papaya*, *L.* and calls it a superposed leaf. This superposed leaf of *Carica Papaya*, *Linn.* as mentioned by him (1), and the "double deck" leaves of the same plant as described by Cook (2), seem to be nothing else but instances of pleiophylly in simple leaves, where the extra leaf arises from the apex of the petiole. Cook (2) regards such "double-deck" leaves, as illustrating the probable manner in which compound leaves have originated from simple ones. This theory is certainly not applicable in those cases where extra leaflets are found on compound leaves, and, as in this instance, on a palmately compound leaf. It is better therefore to record all such cases of extra leaflets, whether on simple or on compound leaves, as merely instances of pleiophylly.

*Dichotomous branching in the Leaves
of*

Gaillardia pulchella, *Fouger*, *N. O. Compositae*

The normal leaves of *Gaillardia pulchella*, *Fouger* are simple dissected ones, and each segment may be partite or sect. (Plate 1, fig. 2, a). There is a prominent midrib running from the base to the apex, which gives off branches to each lobe. In the present case, in some specimens of the species collected from the Victoria Gardens, Bombay, in January 1939, forked leaves were found along with the normal simple leaves on two or three plants, in a bed of about 400 plants. The degree of forking varied with different individuals. Some were forked at the summit, others were partially forked from the middle of the lamina, but none were completely forked from the base. Each lobe of the forked leaf was provided with a prominent midrib. Thus, in these specimens, the venation instead of being of the racemose type, was cymose. The midrib continued half way in most cases, before branching into equally prominent ribs. Each of these daughter axes gave rise to tertiary branches, which developed winged expansions. Thus, each forked vein developed a separate lobe of its own. The size of the lobes of the forked leaves also varied. In some cases one was definitely smaller than the other (Plate 1, Fig. 2, b), in others the difference was not very pronounced (Plate 1, Fig. 2, c) and in a few cases (Plate 1, Fig. 2, d and e) the lobes were identical in size and shape.

Similar instances of forking have been seen in *Anacardium occidentale*, *L.* and in one of the cotyledons of *Michelia Champaka*, *L.* (9), in the leaves of *Aralia Guilfuylei* (10),

Mirabilis jalapa, Linn. (12), Dipsacus fullonum (15), Oleander (7), Scabiosa and Cerastium (14) and Ulmus (6). In other cases, as in Arum maculatum and the garden Pelargonium (6), division has been noted right at the base, so that the two lobes appear as distinct leaflets each provided with its petiole, and arising from a common stalk.

There are two possible explanations of this phenomenon. It may be the result of forking, or of an incomplete union of two leaves. It is not an example of the latter, because in cases of fusion, the number of the midribs indicates the number of fused leaves. In this case, however, there is only one midrib. Hence we have to regard it as a case of forking.

In the case of leaves, fission or forking may be brought about by—

(a) changes in the normal mode of development and growth of the member, caused by some physiological activity, such as the greater and more rapid development of the vascular tissue as compared with the cellular tissue, or

(b) the arrest of the apical meristem, caused either by the attack of insects or fungi, or

(c) some external factors as wind, rain, etc.

In the case under discussion there has been greater development of vascular tissue and the forking of the midrib has taken place. Consequently the configuration of the leaf has been affected. This view is further supported by Goebel (5) and others who have shown that there is a definite relationship between the shape and form of the leaf and its vascular distribution or venation.

Syncarpy in Cucumis sativus, L., N. O. Cucurbitaceae.

The term syncarpy is used to designate the union of the carpels of either a single flower, or between the carpels of different flowers. The union takes place in various degrees. Sometimes only the stalks may be joined, at other times the union extends to part of the fruit or even to its whole extent. Syncarpy is a common phenomenon among flowers with inferior ovaries. The union of two, three and four cucumbers (Plate 2, fig. 3) was first observed by the authors in the vegetable market in Bombay about March 1938, and such fused specimens were later seen very often. When syncarpy takes place between two carpels, usually the united fruits are almost equal in size, but sometimes they may differ in size. One of the two is definitely

larger than the other. In the present instance, both the types were found. There were double fruits of cucumber united from their stalks along their whole length, except at their extremities. In these double fruits, there were some, where both the fruits were straight and of equal length (Plate 2, Fig. 3, b); in others, the fruits were curved and of unequal length (Plate 2 Fig. 3, a). The curvature may be due to the unequal growth rate of the two fusing fruits. When transverse sections of such double fruits were examined, it was found that each of the fused fruits resembled a normal one *viz.*, it had three parietal placentas (Plate 2, Fig. 4, b) with four ovules attached to each, except in one specimen, where there were four placentas (Plate 2 Fig. 4, a) instead of three. Similar examples of syncarpy in Cucumbers have been mentioned by Masters (6), but he noted syncarpy of two fruits only, both being curved and differing greatly in size and structure. Further, one of them was three-celled and the other was one-celled. The specimens collected by the authors deviate from those of Masters (6) in the following respects:—(1) Specimens were both of equal and unequal size, (2) they were straight as well as curved, (3) Syncarpy was not only between two carpels, but between more than two, *viz.*, three and four (Plate 2, Fig. 3, c), and (4) the structure of the united carpels was the same as the normal one in all cases, except in one instance where it was four-celled (Plate 2, Fig. 4, a).

Syncarpy has also been reported in Cherries, Peaches, Gourds, Melons, Hazel-nuts and other popular fruits (6). It may be either due to the failure of separation or of the union of parts originally distinct and separate. It is difficult to attribute syncarpy definitely to either of these two causes. The successive stages in the development of the flower have to be carefully studied before coming to any definite conclusion, as when the floral whorls disappear, it is difficult to determine whether these carpels were formed in one flower, or whether they were the result of the fusion of several flowers. It is also essential to examine the peduncles for traces of fusion in the latter case. In *Cucumis sativus*, L. (4), the female flowers are solitary, but occasionally they may occur in groups. In these abnormal specimens, the scars of the fallen peduncles were examined, and it was found that there were definite constrictions on them, showing thereby, that the abnormality was the result of the fusion of distinct flowers.

Syncarpy in Capsicum annum, L., N. O. Solanaceae.

A similar double fruit of *Capsicum annum*, L. was collected

from the Institute Garden. The two fruits were unequal in size, and were united only in the region of the peduncles and calyces, the actual fruits being almost free (Plate 2, Fig. 5). Here it was easy to conclude that syncarpy between the carpels of two distinct flowers had taken place. The union of the peduncles was evident. The peduncle was flat and expanded laterally, and clearly showed a deep groove along the line of fusion. The calyx lobes at the base of the flower were also increased in number.

Syncarpy in Solanum Melongena, L., N. O. Solanaceae.

Double, triple and multiple fruits of Brinjal were collected from the vegetable market of Bombay. Double fruits are of common occurrence in this species. But here, triple and multiple fruits have been seen (Plate 2, Fig. 6). The fusion in all cases is complete, extending along the whole length of the fruit. The compound fruit showed at the apex of each of its component parts, a distinct scar left by the fallen style. The grooved peduncle, the increased calyx lobes and the remains of the styles on the fruit, lead one to the same conclusion as in the two preceding cases, *viz.*, that these fruits were formed by the fusion of the pistils of a number of flowers.

SUMMARY

The following examples of morphological aberrations have been described and discussed :—

1. Pleiophylly in *Crataeva religiosa*, *Forst* shown by an additional leaflet interpolated above the normal three leaflets,
2. Dichotomous branching in the leaves of *Gaillardia pulchella*, *Fouger*, arising as a result of forking, there being no indications of fusion, and
3. Syncarpy in *Cucumis sativus*, *L.*, *Capsicum annum*, *L.*, and *Solanum Melongena*, *L.*, as a result of the fusion of two or more carpels.

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PLATE I



FIG. 1

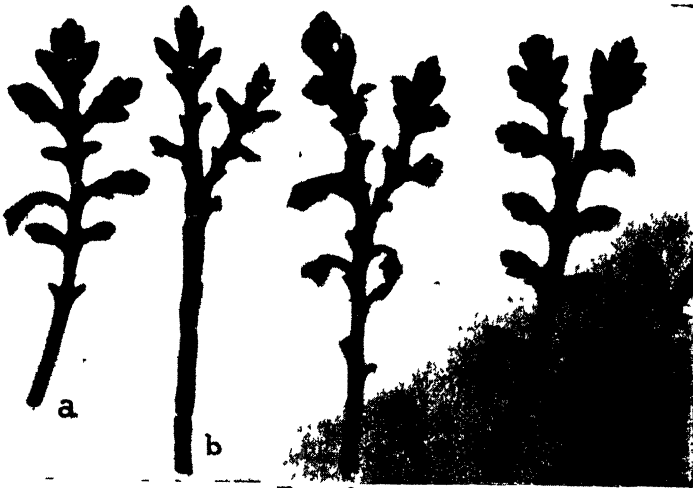


FIG. 2

Fig. 1. Leaves of *Crataeva religiosa*, *Forst.*

- (a) Normal leaf.
- (b) An abnormal leaf with a fourth bilobed leaflet.
- (c) An abnormal leaf with a fourth simple leaflet.

Fig. 2. Leaves of *Gaillardia pulchella*, *Fougier.*

- (a) Normal leaf.
- (b) Dichotomously branched leaf with two unequal lobes, one definitely smaller than the other.
- (c) Dichotomously branched leaf with two unequal lobes, but the difference is not pronounced.
- (d and e) Dichotomously branched leaves with two equal lobes.

PLATE II

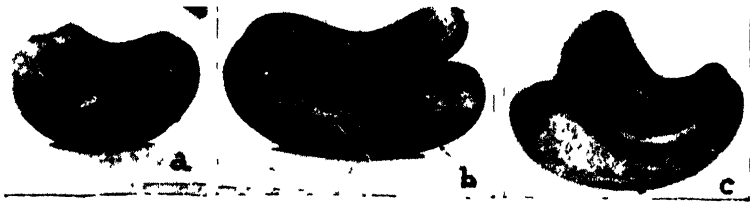


FIG. 3

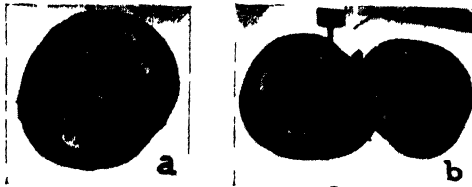


FIG. 4



FIG. 5

FIG. 6

Fig. 3. Syncarpy in *Cucumis sativus*, *L.*

- (a) Double fruit of unequal size and curved.
- (b) Double fruit of almost equal size and practically straight.
- (c) Triple fruit.

Fig. 4. Sections of the fruits.

- (a) Transverse section of the fruit, showing four placentas instead of three, (the other fusing fruit has been removed).
- (b) Transverse sections of fused fruit showing normal placentation.

Fig. 5. Double fruit of *Capsicum annuum*, *L.*

Fig. 6. Syncarpy in *Solanum Melongena*, *L.*

- (a) Double fruit.
- (b) Triple fruit.

NATURAL CROSS-FERTILIZATION IN *LINUM USITATISSIMUM* L. (Linseed) IN THE BOMBAY DECCAN

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INTRODUCTION

Natural cross-fertilization in *Linum usitatissimum* L. has been observed by many workers in the different linseed growing countries. Eyre and Smith (1916) found that in *L. pallascens* white-flowered unbagged plants segregated for white and blue flower colours but no such splitting was noticed in blue-flowered parent cultures. Similarly in *L. humile*, the seed of dark blue and white-flowered types gave rise to progenies having flower colour similar to their respective parents. But the pale blue-flowered types produced mixed progeny consisting of dark blue, pale blue and white-flowered types. From a study of several plant characters of the Indian seed flaxes Howard et al (1919) came to the conclusion that natural crossing is more common in Indian flaxes than would be supposed from the study of the flower.

Henry and Tu (1928) experimentally determined the amount of natural crossing occurring between blue and white-flowered varieties of seed flax grown in adjacent rows sown one foot apart. The percentage was found to vary from 1.25 in 1924 to 1.17 in 1925 as judged by the number of blue-flowered rogues in a white-flowered variety. It was further observed that the percentage of natural crossing in linseed varied inversely with the distance between the rows. The percentage fell from 1.26 to 0.33 as the distance increased from one to five feet. Robinson (1937) studied the extent of natural crossing in blue and white-flowered types grown in adjacent rows and found that it varied from 5 to 6 per cent. in Michigan and 1 to 2 per cent. in

Oregon in U. S. A. He further observed that there was more natural cross-pollination in blue than in white-flowered types. Dillman (1938) observed variations in uniformity, from year to year, of single line selections of flax varieties. His studies have led him to suggest that natural crossing in flax depends on the shape of the flower. The open disc type being more cross-pollinated than the partially closed tubular type and that pollination is further influenced by weather. Freshness and abundance of pollen and the position of anther in respect to stigma considerably affect natural crossing. "Breaking" of types and "degeneration" of flax as a result of mixed planting is a general complaint of flax growers in Holland and Germany. This suggests that natural crossing does occur in fibre flax to some extent.

Kadam et al (1938) working at Niphad, in Bombay Province, observed 3 per cent. crossing on an average when the plants were spaced 4 inches in rows 18 inches apart. The authors of the present paper working on linseed for a number of years at Poona, whose climate is nearly the same as that of Niphad, have obtained somewhat different results which are discussed below.

EXPERIMENTAL

Natural-crossing in linseed was determined under (i) close spacing and (ii) wide spacing conditions.

(i) *Natural-crossing under close spacing.*—During the rabi season of 1934-35 a linseed plot was selected at the College of Agriculture, Poona, which had been drilled with seed one foot apart between the rows and $\frac{1}{2}$ to $\frac{3}{4}$ inch within the row. Six centres from this plot were chosen at random having at each centre a single white-flowered plant surrounded by three to four blue-flowered ones. These were labelled and their seeds separately harvested at maturity. In the following year the progenies of the selected plants were grown in plant to row cultures and the segregation among them for flower colour is given below :—

TABLE I

Segregation of white and blue-flowered linseed types for flower colour when plants were spaced $\frac{1}{2}$ " to $\frac{3}{4}$ " in rows 12" apart

Vicinity centre	Culture number	Flower colour of original plant	White-flowered progeny	Blue progeny	Total plants
1	1	White	30	11	41
	2	Blue	...	32	32
	3	Blue	1	27	28
	4	Blue	...	48	48
2	5	White	47	3	50
	6	Blue	...	46	46
	7	Blue	...	37	37
3	8	White	21	1	22
	9	Blue	...	90	90
	10	Blue	...	53	53
4	11	Blue	...	47	47
	12	White	48	...	48
	13	Blue	1	47	48
	14	Blue	1	41	42
	15	Blue	4	47	51
	16	Blue	...	58	58
5	17	White	29	1	30
	18	Blue	1	23	24
	19	Blue	...	44	44
6	20	White	18	9	27
	21	Blue	...	21	31
	22	Blue	...	35	35
	23	Blue	...	25	25
	24	Blue	...	41	41
Total ...			200	...	...
Blue			7	...	...

From the above table it will be observed that the progeny of white-flowered plants has segregated for flower colour while among the blue-flowered plants some have segregated and others have not. Out of a total of 218 progenies from the white parents 25 are blue-flowered and among 732 progenies of the blue-flowered parents only 7 are white-flowered. Thus out of a total 950 progenies, 32 are off-types giving 3.4 per cent. natural crossing under very close spacing and open pollinated conditions.

(ii) *Natural crossing under wide spacing.*—In order to test the effect of wider spacing on natural crossing in linseed an experiment was laid out in 1936 in which a small square 10' × 10' of white-flowered plants was surrounded by a larger square 100' × 100' of blue-flowered ones. In both, the plants were spaced one foot apart both length- and breadth-wise. There were 100 white-flowered plants in the inner square and 900 blue-flowered ones in the outer. Eleven white-flowered and 43 blue-flowered plants were selected at random from the entire plot and their seeds were separately harvested at maturity. Seeds of the selected plants were grown in progeny rows in the succeeding year and the numbers of off-coloured types which appeared in each culture are given below :—

TABLE II

Segregation for flower colour of white and blue-flowered linseed types when spaced 12" apart both length- and breadth-wise.

Culture number	Petal colour of original plant	White-flowered progeny.	Blue-flowered progeny	Total
1	White	69	...	69
2	White	92	1	93
3	White	126	...	126
4	White	48	1	49
5	White	162	...	162
6	White	148	1	149
7	White	74	...	74
8	White	123	1	124
9	White	86	...	86
10	White	230	2	232
11	White	99	...	99
		1207	6	1213
12	Blue	...	44	44
13	Blue	...	104	104
14	Blue	...	67	67
15	Blue	...	142	142
16	Blue	...	227	227
17	Blue	...	39	39
18	Blue	...	196	196
19	Blue	...	188	188
20	Blue	...	126	126
21	Blue	...	207	207
22	Blue	...	202	202
23	Blue	...	185	185
24	Blue	...	190	190
25	Blue	...	160	160
26	Blue	...	204	204
27	Blue	...	135	135
28	Blue	...	201	201
29	Blue	...	165	165
30	Blue	...	199	199
31	Blue	...	208	208
32	Blue	...	145	145
33	Blue	...	153	153
34	Blue	...	236	236
35	Blue	...	174	174
36	Blue	...	259	259
37	Blue	...	287	287
38	Blue	...	224	224
39	Blue	...	234	234
40	Blue	...	104	104
41	Blue	...	235	235
42	Blue	...	114	114
43	Blue	...	92	92
44	Blue	...	111	111
45	Blue	...	106	106
46	Blue	...	108	108
47	Blue	...	186	186
48	Blue	...	188	188
49	Blue	...	156	156
50	Blue	...	125	125
51	Blue	...	99	99
52	Blue	...	158	158
53	Blue	...	140	140
54	Blue	...	114	114

It will be observed from the above table that there is segregation for flower colour in the progenies of white-flowered parents only and no segregation amongst the blue-flowered ones. Therefore, in determining natural crossing only the progenies of eleven white-flowered types from the inner square are considered here. Out of a total 1213 plants 1207 are white and 6 are blue-flowered thus giving 0.58 per cent. natural crossing under wider spacing.

DISCUSSION

The foregoing two experiments with respect to the effect of spacing on natural cross-fertilization show that closer the spacing greater is the natural crossing. This result confirms the observation of Henry and Tu (1928). The spacing adopted by Kadam et al is 4" in rows 18" apart while that of the present authors is $\frac{1}{2}$ " to $\frac{3}{4}$ " in rows 12" apart. Thus the spacing given by Kadam et al is wider both within and between the rows by $3\frac{1}{2}$ " to $3\frac{1}{4}$ " and 6" respectively. The average percentage of natural crossing observed by Kadam. et al is 3 per cent. at Niphad which is nearly equal to 3.4 per cent observed by present authors under much closer spacing at Poona. Since the climates at Niphad and Poona are more or less similar it is expected that wider spacing should result in lesser natural crossing at Niphad. Since this is not the case it would appear that there are other factors besides spacing, which influence natural crossing in linseed.

CONCLUSION

(1) There is an inverse relationship between spacing and extent of natural crossing in linseed. Closer spacing increases natural crossing.

(2) At Poona in the Bombay Deccan 3.4 per cent natural crossing occurs when plants are spaced $\frac{1}{2}$ " to $\frac{3}{4}$ " in rows 12" apart. But when the spacing is increased 12" all round, the natural crossing is reduced to 0.58 per cent.

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STUDIES IN HAEMOLYSIS*

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The present investigation was undertaken to determine, by a statistical study, whether any relationship exists, firstly, between the fragility (osmotic resistance) of human erythrocytes in saline solution and the various factors of blood such as the size and number of the red corpuscles, their haemoglobin content, their volume, thickness etc.; and secondly, between these various factors themselves.

With this end in view the haemolysis of erythrocytes in thirty samples of blood was noted against sodium chloride solutions of different strengths. The haemoglobin content, R. B. C. count, corpuscular volume, and the corpuscular size in each sample were also determined. From these data other factors such as the mean corpuscular volume (M. C. V.), the average corpuscular haemoglobin, the mean corpuscular haemoglobin concentration (M. C. H. C.), and the mean corpuscular average thickness (M. C. A. T.) were calculated.

The data thus obtained were tabulated and the coefficients of correlation between pairs of these various factors were then computed by the usual statistical methods.

METHODS

The following methods were used in this study :—

(a) *Samples of blood.*—These were obtained from subjects attending the Sir J. J. Hospital, Bombay, for such surgical complaints as hydrocele, hernia etc. which presumably may not be affecting the physiological condition of blood to any appreciable extent.

Blood was drawn from one of the veins at the front of the elbow and immediately added to half a c.c. of a 3 per cent.

* The expenses of this research were partly met from a research grant received from the University of Bombay in 1937-38.

solution of sodium citrate contained in a small test tube. The tube was marked at the 5 c.c. level and the blood was added upto this mark. The blood and citrate were then gently mixed together by inversion. It was then carried to the laboratory for examination which was done immediately afterwards.

(b) *Osmotic resistance (fragility) of erythrocytes.*—An accurately made one per cent. solution of pure sodium chloride (Merck) was used as a stock solution. This was checked against a standard silver nitrate solution by titration from time to time.

A series of twenty-two $3 \times \frac{1}{2}$ in. test tubes was placed in a rack and numbered. The sodium chloride solution (1%) was measured from a 5 c.c. microburette into these tubes from nos. 1 to 21 in diminishing amounts beginning with 1.5 c.c. in no. 1 to 0.5 c.c. in tube no. 21, each successive amount diminishing by 0.05 c.c.,—thus 1.5 c.c. in the first tube, 1.45 c.c. in the second, 1.4 c.c. in the third and so on.

From another 5 c.c. microburette distilled water was then added to each tube beginning with 1 c.c. into the first tube to 2 c.c. in the twenty-first, each successive amount increasing by 0.05 c.c.,—thus 1 c.c. in tube no. 1, 1.05 c.c. in no. 2, 1.1 c.c. in no. 3 and so on.

The two were then thoroughly mixed together in each tube by inversion against the thumb and index finger. The resulting solutions in the tubes were thus made to vary in strength from 0.60 per cent. in the first tube to 0.20 per cent. in the 21st—each successive solution diminishing in strength by 0.02 per cent., the total volume of fluid in every tube remaining the same *viz.* 2.5 c.c. The last tube (no. 22) was used as a control with 2.5 c.c. of plain distilled water placed in it.

20 c.mm. of the evenly mixed citrated blood, accurately measured by a haemoglobinometer pipette, was then emptied thoroughly into each of the twenty-two tubes by drawing it in and out two or three times. After each addition the blood was mixed with the saline by gentle inversion.

The rack of tubes was set aside and after half an hour the tube in which the haemolysis had been just complete was noted and the strength of the solution recorded. In each case the completion of haemolysis was confirmed by noting the absence of red cells in the mixture on microscopical examination.

(c) *Haemoglobin.*—This was estimated by the usual Haldane haemoglobinometer method. Coal gas formed the source of carbon monoxide.

(d) *R. B. C. count.*—This was done with a Thoma haemocytometer and chamber. In every case the blood was diluted 1 in 200 with Hayem's solution, the corpuscles in eighty small squares were counted, and then calculated in millions per c.mm.

(e) *Relative corpuscular volume.*—This was determined by Wintrobe's method (4). The special Wintrobe haematocrite tube (length 11 c.m.; bore 2.5 mm.; graduated with a centimeter-millimeter scale 10 c.m. in length) filled with the citrated blood by the capillary pipette was centrifugalised in a rapid centrifuge machine (Phillips Drucker's) with 3000 to 4000 revolutions per minute for an hour. Repeated observations were made from time to time to see whether the duration of centrifugalisation had any effect on the constancy of the cell volume but in no case was any change in the level of the corpuscles noted after the first fifteen minutes. However the final reading for record was always taken at the end of at least one hour's centrifugalisation.

The volume of packed red cells was read off directly from the Wintrobe tube and recorded as the number of c.c. of cells per 100 c.c. of blood.

(f) *Size of R. B. C. (Mean Corpuscular Diameter, M.C.D.).*—This was estimated by the diffraction method using the Direct Halometer manufactured by Allen & Hanburys Ltd., London. This is a portable instrument easy to handle and consists of an outer metal casing with a sliding tube telescoped inside as in a pocket spectroscope. A thin evenly spread blood film is viewed through a peephole at the end of the instrument against light. There is an arrangement inside by which the source of light is reflected from two inclined mirrors to give two beams of light. Two rings of halo-spectra are thus seen as a result of diffraction through the blood film. The inner sliding tube is moved out or inwards until the two red rings of the spectra just touch each other. The instrument is calibrated to give the relation between this position of the light and the mean diameter (modal and not the arithmetic mean) of the cells in microns (μ).

The size of the corpuscles is thus read directly on the scale given on the inner tube. The average of several readings from each of two blood films of every sample was taken to represent the size of the corpuscles in microns (μ).

(g) *Mean corpuscular haemoglobin (colour index in $\gamma\gamma$) (4).*—The absolute value corresponding with the usual colour index is known as the mean corpuscular haemoglobin. This expresses

the average haemoglobin content of a single red cell in micromicrograms ($\gamma\gamma$).

This was obtained thus :—

$$\left(\frac{\text{Haemoglobin in grms. per 1000 c.c. of blood}}{\text{Red cells in millions per c.mm. (d above)}} \right) \gamma\gamma.$$

For the purposes of this calculation, since the haemoglobin estimation was done by the Haldane method (see *c* above), the percentage result was converted into gms. at 13.8 gms. per 100 c.c. of blood.

(h) *Mean corpuscular haemoglobin concentration (M. C. H. C.)* (4).—This expresses the relation between the haemoglobin saturation and the cell volume. It takes no account of the number of red cells. The degree of saturation is expressed by stating the haemoglobin in gms. per cent. as a percentage of the cell volume in c.c. per cent., *i.e.*, the amount of haemoglobin per 100 c.c. of cells as distinct from whole blood. It is a true indicator of the iron content of the red cells.

It was calculated as follows :—

$$\frac{\text{Haemoglobin in gms. per 100 c.c. of blood}}{\text{Volume of packed red cells in c.c. per 100 c.c. of blood (e above)}}.$$

For this purpose again the haemoglobin as determined in (*c*) above was converted into gms. at 13.8 gms. per hundred c.c. of blood.

(i) *Mean corpuscular volume (M. C. V.)* (4).—This is the mean volume of a single red cell expressed in cubic microns (*c.μ*) and gives the dimensions of the cell in all planes and not only in the long axis as in diameter measurements (*f* above).

It was obtained thus :—

$$\left(\frac{\text{Volume of packed cells in 100 c.c. blood (e above)} \times 10}{\text{Red cells in millions per c.mm. (d above)}} \right) \text{c.}\mu.$$

(j) *Mean corpuscular average thickness (M. C. A. T.)* (4).—The normal red cell being biconcave in shape its thickness obviously varies at different points; hence it is possible only to estimate its average thickness. This is calculated by assuming that the cell on edge has the form of a cylinder. Having made this assumption the ordinary formula for finding out the volume of the cylinder is applied *viz.* volume = area $\times$ height, or that is,

$$\begin{aligned} \text{height} &= \frac{\text{volume}}{\text{area}} = \frac{\text{volume}}{\pi r^2} \\ &= \left(\frac{\text{Mean corpuscular volume (M. C. V.)}}{\pi \left(\frac{\text{Mean corpuscular diameter (M.C.D.)}}{2} \right)^2} \right) \text{microns } (\mu). \end{aligned}$$

The M. C. V. and M. C. D. having been found in (i) and (f) above respectively the final calculation of the thickness was thus very easy.

(k) *Statistical methods for describing and correlating the above factors* (1).—The data obtained by the examination of the blood samples and by the calculation of the other factors given above were tabulated and then subjected to the following statistical study:—

The frequency distribution of each factor was worked out by the group computation technique. The mean (M) and the standard deviation (σ) were found out and their probable errors (P. E.) calculated by the following formulae:—

$$\text{P. E. of Mean (M)} = \frac{1}{3} \left(\frac{\sigma}{\sqrt{n-1}} \right)$$

$$\text{and P. E. of standard deviation } (\sigma) = \frac{1}{3} \left(\frac{\sigma}{\sqrt{2(n-1)}} \right).$$

(Note.— n denotes the size of the sample, here 30).

For the determination of the coefficient of variation (c. of v.) per cent. the formula used was $\frac{100\sigma}{M}$.

The computation of the correlation coefficient (r) between the different pairs of the tabulated data was performed by arranging them into correlation tables. The probable error of the correlation coefficient (P. E. $_r$) was computed by the formula

$$\frac{1}{3} \left(\frac{1-r^2}{\sqrt{n-2}} \right).$$

RESULTS

The data about the factors obtained by observation and calculation as mentioned above are given in Table I. The serial order follows the size of the corpuscles:—

TABLE I

Observed and calculated factors of blood samples

Serial No.	NaCl Sol. p. c. for complete hæmolysis	Hæmoglobin p. c. (Haldane method)	R. B. C. millions per c.mm.	Relative corpuscular volume p. c. (Wintrobe method)	Mean size of R. B. C. (M. C. D.) in μ	Mean corpuscular hæmoglobin in $\gamma\gamma$	Mean corpuscular hæmoglobin concentration (M. C. H. C.)	Mean corpuscular volume (M. C. V.) in c. μ	Mean corpuscular average thickness (M. C. A. T.) in μ
1	0.38	58	3.7	25	8.3	22	32	68	1.3
2	0.34	75	4.2	40	8.2	25	26	95	1.8
3	0.36	70	4	38	8.2	24	25	95	1.8
4	0.34	68	3.8	32	8.1	23	29	84	1.6
5	0.36	80	4	38	8.1	28	29	95	1.8
6	0.34	58	4.8	40	8.1	17	20	83	1.6
7	0.32	76	4.2	36	7.9	25	29	86	1.8
8	0.34	78	3.8	34	7.9	28	32	89	1.8
9	0.34	80	5.4	36	7.8	20	31	67	1.4
10	0.34	66	5	45	7.8	18	20	90	1.9
11	0.38	90	5.2	40	7.8	24	31	77	1.6
12	0.34	75	4.5	40	7.8	23	26	89	1.9
13	0.34	80	4.2	38	7.75	26	29	90	1.9
14	0.34	72	4	36	7.7	25	28	90	1.9
15	0.38	76	4.6	42	7.7	23	25	91	2
16	0.36	76	5.5	45	7.7	19	23	82	1.8
17	0.38	80	4.2	38	7.7	26	29	90	1.9
18	0.42	75	3.5	36	7.7	30	29	103	2.2
19	0.36	67	7	31	7.65	13	30	44	1
20	0.40	75	5	46	7.65	21	23	92	2
21	0.34	65	5.2	40	7.65	17	22	77	1.7
22	0.34	70	4.2	38	7.65	23	25	90	2
23	0.30	70	5.6	32	7.65	17	30	57	1.2
24	0.36	66	4.5	42	7.6	19	22	93	2
25	0.34	70	3.6	35	7.5	27	28	97	2.2
26	0.34	80	4	38	7.5	28	29	95	2.1
27	0.36	70	5.6	38	7.5	17	25	68	1.5
28	0.36	78	5.2	42	7.4	21	26	81	1.9
29	0.38	90	5.6	45	7.3	22	28	80	1.9
30	0.38	84	4.4	40	7.3	26	29	91	2.2

It will be seen that the strength of saline in which the maximum hæmolysis occurred varied from 0.30 to 0.42 per cent.

showing that the erythrocytes differed widely in their osmotic resistance.

The hæmoglobin percentage of the samples ranged from 58 to 90 by the Haldane method and the R. B. C. count from 3.5 to 7 millions per c.mm. The average corpuscular hæmoglobin content calculated from these showed a variation from 13 to 30 micromicrograms ($\gamma\gamma$).

While the corpuscular volume relative to the whole blood fluctuated from 25 to 46 per cent. the mean volume of the individual cells fluctuated equally widely from 44 to 103.

The range of the mean hæmoglobin concentration in the cells was 20 to 32 per cent.

The average size of the red cells will be seen to have been from 7.3 to 8.3 μ . It is said that the size of the cells in the "wet" state as suspended in the plasma is greater than that obtained from a film on drying as drying leads to shrinkage (3) but this was the only method available here for this determination. Besides such relative values should serve equally well for the purposes of statistical correlation.

The average thickness of the cells varied from 1 to 2.2 μ .

The descriptive constants which were computed statistically from these data are summarised in Table II. It shows that the frequency distribution of the samples is fair. The coefficients of variation are also very low.

TABLE II
Statistical descriptive constants of data in Table I

Data	Mean $\pm$ P.E. _m	Standard deviation (σ) $\pm$ P.E. _{σ}	Coefficient of variation (c. of v.) p.c.
NaCl Sol. p. c. for complete hæmolysis	0.36 $\pm$ 0.003	0.024 $\pm$ 0.002	6.6 p. c.
Hæmoglobin p. c. (Haldane method)	72.67 $\pm$ 0.896	7.245 $\pm$ 0.634	10 p. c.
R. B. C. millions per c. mm.	4.6 $\pm$ 0.103	0.834 $\pm$ 0.073	18 p. c.
Relative corpuscular volume p. c. (Wintrobe method)	37.9 $\pm$ 0.584	4.724 $\pm$ 0.413	12 p. c.
Mean size of R. B. C. (M. C. D.) in μ	7.75 $\pm$ 0.032	0.26 $\pm$ 0.022	3.3 p. c.
Mean corpuscular hæmoglobin in $\gamma\gamma$	22.09 $\pm$ 0.495	4.005 $\pm$ 0.350	18 p. c.
Mean corpuscular hæmoglobin concentration (M. C. H. C.)	26.5 $\pm$ 0.427	3.452 $\pm$ 0.302	13 p. c.
Mean corpuscular volume (M. C. V.) in c. μ	83.33 $\pm$ 1.63	13.19 $\pm$ 1.15	16 p. c.
Mean corpuscular average thickness (M. C. A. T.) in μ	1.78 $\pm$ 0.036	0.292 $\pm$ 0.025	16 p. c.

In Table III are given the coefficients of correlation obtained between the various pairs of data in Table I.

TABLE III

Coefficients of correlation computed between different pairs of data in Table I

Data	Correlation coefficient (r) with P.E. $\pm$
NaCl Sol. p. c. for complete hæmolysis and hæmoglobin percentage by Haldane method	$+0.25 \pm 0.11$
NaCl Sol. p. c. for complete hæmolysis and R. B. C. millions per c.mm.	-0.04 ± 0.12
NaCl Sol. p. c. for complete hæmolysis and relative corpuscular volume p. c.	$+0.23 \pm 0.12$
NaCl Sol. p. c. for complete hæmolysis and mean corpuscular size in μ	-0.11 ± 0.12
NaCl Sol. p.c. for complete hæmolysis and mean corpuscular hæmoglobin in $\gamma\gamma$	$+0.20 \pm 0.12$
NaCl Sol. p. c. for complete hæmolysis and mean corpuscular hæmoglobin concentration	$+0.07 \pm 0.12$
NaCl Sol. p. c. for complete hæmolysis and mean corpuscular volume in c. μ	$+0.29 \pm 0.11$
NaCl Sol. p. c. for complete hæmolysis and mean corpuscular average thickness in μ	$+0.24 \pm 0.12$
Hæmoglobin p. c. (Haldane method) and R. B. C. millions per c. mm.	$+0.10 \pm 0.12$
Hæmoglobin p. c. (Haldane method) and relative corpuscular volume p.c.	$+0.40 \pm 0.10$
Hæmoglobin p. c. (Haldane method) and mean corpuscular size in μ	$+0.35 \pm 0.11$
Hæmoglobin p. c. (Haldane method) and mean corpuscular hæmoglobin in $\gamma\gamma$	$+0.44 \pm 0.10$
Hæmoglobin p. c. (Haldane method) and mean corpuscular hæmoglobin concentration	$+0.45 \pm 0.10$
Hæmoglobin p. c. (Haldane method) and mean corpuscular volume in c. μ	$+0.20 \pm 0.12$
Hæmoglobin p. c. (Haldane method) and mean corpuscular average thickness in μ	$+0.32 \pm 0.11$
R. B. C. millions per c. mm. and relative corpuscular volume p.c.	$+0.22 \pm 0.12$
R. B. C. millions per c. mm. and mean corpuscular size in μ	-0.51 ± 0.09

TABLE III—concl'd.

Data	Correlation coefficient (r) with P. E. $\pm$
R. B. C. millions per c. mm. and mean corpuscular hæmoglobin in $\gamma\gamma$	-0.79 ± 0.04
R. B. C. millions per c. mm. and mean corpuscular hæmoglobin concentration	-0.21 ± 0.12
R. B. C. millions per c. mm. and mean corpuscular volume in c. μ	-0.67 ± 0.07
R. B. C. millions per c. mm. and mean corpuscular average thickness in μ	-0.52 ± 0.09
Relative corpuscular volume p. c. and mean corpuscular size in μ	-0.43 ± 0.10
Relative corpuscular volume p. c. and mean corpuscular hæmoglobin in $\gamma\gamma$	-0.01 ± 0.12
Relative corpuscular volume p. c. and mean corpuscular hæmoglobin concentration	-0.60 ± 0.08
Relative corpuscular volume p. c. and mean corpuscular volume in c. μ	$+0.48 \pm 0.09$
Relative corpuscular volume p. c. and mean corpuscular average thickness in μ	$+0.57 \pm 0.09$
Mean corpuscular size in μ and mean corpuscular hæmoglobin in $\gamma\gamma$	$+0.17 \pm 0.12$
Mean corpuscular size in μ and mean corpuscular hæmoglobin concentration.	$+0.12 \pm 0.12$
Mean corpuscular size in μ and mean corpuscular volume in c. μ	$+0.12 \pm 0.12$
Mean corpuscular size in μ and mean corpuscular average thickness in μ	-0.30 ± 0.11
Mean corpuscular hæmoglobin in $\gamma\gamma$ and mean corpuscular hæmoglobin concentration.	$+0.49 \pm 0.09$
Mean corpuscular hæmoglobin in $\gamma\gamma$ and mean corpuscular volume in c. μ	$+0.70 \pm 0.06$
Mean corpuscular hæmoglobin in $\gamma\gamma$ and mean corpuscular average thickness in μ	$+0.64 \pm 0.08$
Mean corpuscular hæmoglobin concentration and mean corpuscular volume in c. μ	-0.24 ± 0.12
Mean corpuscular hæmoglobin concentration and mean corpuscular average thickness in μ	$+0.22 \pm 0.12$
Mean corpuscular volume in c. μ and mean corpuscular average thickness in μ	$+0.85 \pm 0.03$

It will be seen that the most significant correlation coefficient obtained in the series is $+0.85$ between the mean corpuscular volume and the mean corpuscular average thickness. Next in order are the negative correlation between the R. B. C. count and the mean corpuscular haemoglobin and the positive correlation between the average corpuscular haemoglobin and the average corpuscular volume. The negative correlation between the R. B. C. count and the average corpuscular haemoglobin and the positive one between the mean corpuscular haemoglobin and the mean average thickness of a cell follow closely upon these and all of them considered together seem to be of some definite physiological significance.

CONCLUSIONS

A study of the correlation coefficients between the factors considered leads one to draw the following conclusions:—

(1) The Osmotic resistance (fragility) of the red cells bears no relationship whatsoever to any of the other factors. It is said that the fragility of the red cells to saline solutions is intimately bound up with the shape and size of the cells, that the lesser the mean corpuscular diameter and the mean corpuscular volume the greater the resistance and *vice versa*, that the more spherical the corpuscle the more the fragility to saline etc. This has been concluded from observations on the resistance of cells of different animals and of man (4). In support of this statement is also mentioned the significance of the greater thickness of the erythrocytes than normal in acholuric jaundice where, it is now sufficiently well known, the fragility is increased.

The present study however does not bear out these views. It may be that amongst human erythrocytes themselves, which are otherwise normal, variations in size and shape have no effect on the fragility.

(2) The percentage of haemoglobin in blood as estimated by the Haldane method has no relationship with the other factors. If at all one may say there is very slight correlation between this figure and the average haemoglobin content of a single cell or the average haemoglobin saturation of the volume of red cells.

(3) The R. B. C. count has an appreciably high negative correlation with the average haemoglobin content of a single cell and with the average volume of a single red cell. This may mean that as the number of cells is increased in the blood the haemoglobin content and/or the volume of each individual

cell is decreased and *vice versa*. If it be so may this not suggest that it is one means of adjustment by which the system tries to keep the total haemoglobin content of the blood as constant as possible? For this might ensure the same oxygen carrying capacity of the blood as before at the same time ensuring also the prevention of occurrence of any bad consequences resulting from too high a concentration of haemoglobin in the blood such as, for example, from any increase in the viscosity of the blood which in its turn might diminish the velocity of circulation, increase the peripheral resistance and blood pressure etc., The same amount of haemoglobin spread over a greater number of cells may also mean greater ease of gaseous exchange in the body.

There is also some negative correlation though less appreciable between the count and the average corpuscular size and the average corpuscular thickness. This is to be expected on the above presumption and well bears out the possible explanation since it may be held that the size and the thickness decrease to hold less haemoglobin per cell as the total number of cells increases in the blood.

(4) There is a negative correlation between the relative cell volume per cent. and the average haemoglobin saturation; that is to say as the cell volume increases the mean corpuscular haemoglobin concentration goes down. As the latter factor is a true indicator of the iron content (*i.e.* haemoglobin) of the cells this may also go to support the above contention that as the cell volume increases the haemoglobin saturation goes down thus keeping the total haemoglobin content in the cells practically constant.

The cell volume seems to show some positive correlation with the average thickness of a cell. This is as it should be so that the greater the thickness of each individual cell the greater is the total volume of cells.

(5) The mean corpuscular size has no definite correlation with any other factor but as has been stated above is negatively correlated with the R. B. C. count.

(6) The average haemoglobin content of a single cell seems to bear a positive relationship both with the average volume and the average thickness of a cell. This is to be expected as with a greater amount of haemoglobin the cell must be greater in capacity and thickness.

It is very slightly related to the average haemoglobin saturation of the cells per cent.

As has been pointed out above it shows a relatively high negative correlation with the R. B. C. count presumably for the reasons discussed there.

(7) The mean corpuscular volume shows a definite and high positive correlation with the average thickness of the cell and none with the average corpuscular diameter (size). Does this suggest that the volume of a cell increases or decreases with its thickness alone and that the diameter of a cell does not vary much in the same individual?

SUMMARY

A statistical study suggests that there is no significant correlation between the fragility of human red cells and any of the factors such as the mean corpuscular size, thickness, volume, haemoglobin content, haemoglobin saturation, red cell count etc. The R. B. C. count shows a negative correlation with the mean corpuscular haemoglobin content and the mean corpuscular volume respectively while the mean corpuscular volume bears a significant positive relationship with the mean corpuscular average thickness. The mean corpuscular haemoglobin and the mean corpuscular volume are also positively correlated.

In concluding this paper, I wish to thank all those surgeons of the Sir J. J. Hospital, Bombay, and the subjects who were kind enough to provide me with the samples of blood.

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A NOTE ON ABNORMALITIES IN CERTAIN PLANTS

(With 5 Plate figures.)

By

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Abnormalities of various plants members are recorded in the scholarly works of Masters (6) and Worsdell (14). Occurrences of abnormalities among Indian plants have been recorded by Sabnis (8), Saran (9), Singh (10 and 11), Sinha (10 and 12), Cooper (2) and others. Study of abnormalities is very interesting from the scientific point of view. Such freaks of nature are now no more considered as freaks or monstrosities, but they are of great value in solving the morphological nature of the various organs of plants.

Abnormalities described in this note were collected either from the College Botanical Garden or from the market at Junagadh.

1. DOUBLE LEAF OF *DIOSCOREA ALATA*, Linn.

N. O. Dioscoreaceae

Dioscorea alata, Linn. is a right handed twinner, the tuberous roots of which are much esteemed as food by people. Its stem is acutely tetragonous and winged. Its leaves are usually opposite, simple, petiolate, sub-bastately or deeply oordate in general outline. The margin of the leaf is entire and the apex of the leaf is cuspidate. The petiole is stout and winged like the stem.

In this plant abnormalities have been recorded by Worsdell (14) in the lateral cotyledon and ringfasciation in the shoots.

An abnormal leaf was noticed by the present writer (Plate-fig. 1). This leaf showed fasciation or union of the petioles of the leaves and also the union of the lower surfaces of the lamina of both the leaves by one of the veins only. The length of the petioles was unequal; one slightly bigger than the other. The ptyxis of the abnormal leaf was observed to be normal *i.e.* conduplicate. In young condition two conduplicate laminae were not free but were united from the lower surfaces

by one of the veins of the inner lobes, leaving the rest of the part quiet free on either side of the union of the veins. The venation is reticulate, multicostate, convergent. There are in all nine veins, one in the centre and four in each lobe. The first vein from the margin in both the lobes (free as well as fused) is further divided into two *i.e.* forked. One of the forked veins of the inner lobe of one leaf is fused along the lower surface to one of the forked veins of the inner lobe of the other leaf. The distance between the fourth vein of both the lobes and the central vein in both the leaves is unequal. The fourth vein of the fused lobe of leaf No. 1 is very near the central vein. The apex of the leaf No. 1 is pointing towards the free lobe while that of the leaf No. 2 is pointing towards the fused lobe.

It seems that the abnormality in question may be due to the spiral torsion caused by the twisting of the stem. The normal arrangement of the leaves on the stem is of opposite type. In the present case due to the torsion caused by the twisting of the stem, the regions which give rise to the leaves are brought very near each other. Thus the leaf which is normally opposite is displaced in such a manner that the two leaves are arranged on one side of the stem only. Besides lateral pressure may be responsible in bringing about the fusion of the petiole, etc.

Goebel (4) has cited cases of "double leaves" on artificially produced fasciated shoots of *Phaseolus multiflorus* and *Vicia Faba*. These are instances of compound leaf while the leaf of *Dioscorea* is a simple one. Masters (6) has cited more or less similar cases of cohesion of petioles only, in the leaves of *Pelargonium*, *Tropaeolum majus* and *Strelitzia Reginae*.

The abnormality in the present case is of quite a different nature from those previously described by various authors (8, 9, 10, 11).

2. DOUBLE CAPITULA OF *HELIANTHUS RIGIDUS*, *Desf.*

N. O. Compositae.

The phenomenon of fasciation of capitula is common among the Compositae, but as far as the writer is aware, no such record has so far been made for *Helianthus rigidus*, *Desf.* In the present case (Plate-fig. 2), the two capitula are seen fused together. The two peduncles are united together, so that the two Capitula are at right angles to the fasciated peduncles.

Fasciation of two Capitula is recorded in *Taraxicum officinale* by Goebel (4); in *Gaillardia pulchella* by Cooper & Gonzalves (2); and in *Cosmos Bipinnatus* by Singh and Sinha (10).

3. SEEDLING OF *HELIANTHUS ANNUUS*, Linn.*N. O. Compositae*

As a rule there are two cotyledons present in Sunflower seedling. Several fruits were germinated for the class work. From these few seedlings were seen having three cotyledons instead of the usual two (Plate-fig. 3). General outline of the cotyledon is more or less semi-elliptical with a broad upper end and a narrow lower one; but in the present case the outline of the cotyledon is not semi-elliptical but is a sector of an ellipse. So in this case an ellipse is divided into three parts of which two are more or less of the same size and shape. Of these few tricotyledonous seedlings, some have two big cotyledons and one small cotyledon; while others have two small cotyledons and one big cotyledon. The normal arrangement of the cotyledons is opposite while in this case there is a whorl of three cotyledons.

Presence of syncotyle is recorded in *Helianthus annuus* by Worsdell (14). In the present case three cotyledons are present. Occurrences of a large number of cotyledons as well as a single cotyledon in Dictoyledonous plants are recorded by various authors (5, 6, 8, 11 and 13). Presence of one or two cotyledons in the embryo is generally accepted as a valuable means of classifying Angiosperms into two primary groups, Monocotyledons and Dicotyledons. So from this, it is clear that the presence of a number of cotyledons in the embryo is not the sole characteristic to be taken into account for classification of plants.

The abnormality in the present case may be due to either the phenomenon of Schizocotyle or to the division of the apical portion of the growing embryo into three, which in the normal course would have given rise to two cotyledons by dividing into two.

4. QUADRUPLE FRUIT OF *MUSA SAPIENTUM*, Linn.*N. O. Musaceae.*

This specimen was purchased from the market at Junagadh. As a rule the fruit is separate but very often two fruits are seen joined together. In this case (Plate-fig. 4), four fruits of greenish yellow skinned variety of Kela are concerned in the syncarpy. Abnormalities in the flowers of *Musa* have been recorded by Agharkar (1). Singh (11), Costrus & Smith (3) and Phillips (7) have described abnormalities in fruits.

Owing to differences in details, an account of the specimen will not be out of place. Of the four fruits, in three there is

complete fusion throughout the whole length forming one bunch. The fourth one is partially fused to this bunch of three. Its apical portion which bears the scar of the fallen floral parts is free while that of the bunch of three is fused.

The examination of its transverse section proved it to be developed from a normal gynæcium. Thus in the present case abnormality is the result of a coalescence of four flowers.

5. DOUBLE BERRY OF COCCINIA INDICA, *Wight and Arn.*

N. O. Cucurbitaceae

The fruits of *Coccinia indica* are eaten as vegetable. The specimen (Plate-fig. 5) was purchased from the market at Junagadh. Two fruits are fused together along their edges lengthwise. Only the apices of the fruits become separated from one another. In length both the fruits are very nearly same *i.e.* 2"; but there is a difference in the breadth. One has breadth of one inch while the other has 0.8". At the base of this fruit there is a scar of the stalk. As the fruits sold in the market are without stalks it is not possible to say that this scar is the result of a single normal stalk or of two fasciated stalks. It is very difficult to decide whether the present abnormal fruit is formed from a single flower or by the fusion of two flowers. In this plant the female flower is solitary. This adds further difficulty in solving the point.

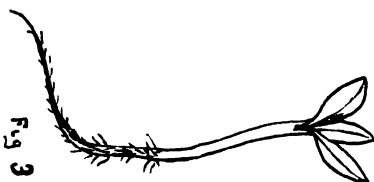
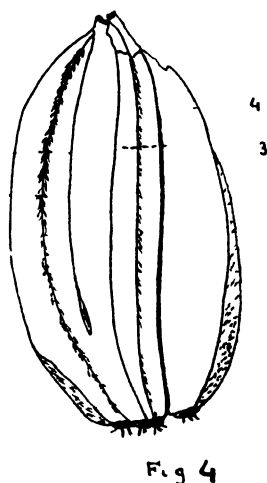
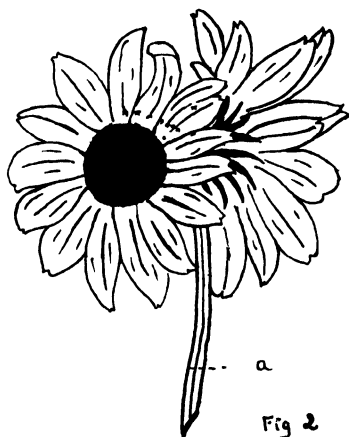
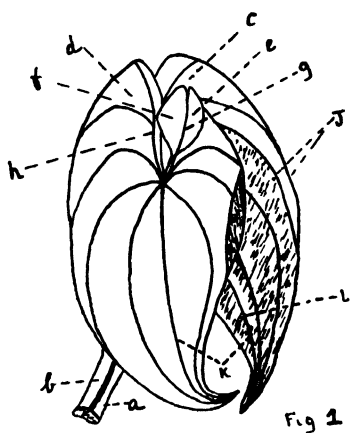
The examination of the transverse section showed normal structure characteristic of Cucurbitaceous type.

A similar type of abnormality is recorded in *Trichosanthes dioica*, *Roxb.* by Sinha (12). Syncarpy among other Cucurbitaceous plants, such as Gourds, Melons and Cucumbers is cited by Masters (6).

SUMMARY

Abnormalities in the following plants are described :—

1. Double leaf of *Dioscorea alata* *Linn.* N. O. Dioscoreaceae.
2. Double capitula of *Helianthus rigidus*, *Desf.* N. O. Compositae.
3. Tricotyledonous seedlings of *Helianthus annuus*, *Linn.* N. O. Compositae.
4. Quadruple fruit of *Musa sapientum*, *Linn.* N. O. Musaceae.
5. Double berry of *Coccinia indica*, *Wight and Arn.* N. O. Cucurbitaceae.



- Fig. 1. Double leaf of *Dioscorea alata*, *Linn*, showing —
 (a & b) Fasciated petioles of leaf No. 1 & 2. (c & d) Free outer lobes of leaf No. 1 & 2. (e & f) Fused inner lobes of leaf No. 1 & 2. (g) Fused vein of inner lobes of leaf No. 1 & 2. (h) Forked vein of the free lobe of leaf No. 2. (i) Margin of leaf No. 1. (l) Central vein of the leaf No. 1 and 2. (l) Fourth vein of the fused lobe of leaf No. 1.
 (Reduced to half the natural size).
- Fig. 2. Double capitula of *Helianthus rigidus*, *Desf.* showing fasciated peduncles (a).
- Fig. 3. Seedling of *Helianthus annuus*, *Linn.* showing three cotyledons.
- Fig. 4. Quadruple fruit of *Musa sapientum*, *Linn.* (Reduced to half the natural size).
- Fig. 5. Double berry of *Coccinia indica*. *Wight and Arn*, showing fused scar of the stalk.

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A SIMPLE COLORIMETRIC METHOD FOR MICRO-DETERMINATION OF SODIUM

By

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In all investigations of saline and alkaline soils sodium plays most prominent part; reactions of sodium in soils and in plants are well known to all soil scientists and agricultural chemists. Recently Mulwani and Pollard (1939) have shown how sodium adversely affects soil conditions and the growth of farm crops. A sodium soil is a real type of alkali soil and is most unsuitable for the germination of seeds and growth of the plants. In presence of water it is deflocculated and consequently presents very undesirable physical properties. The relative impermeability of sodium soils is one of their striking characteristics; and this influence greatly adds to the difficulty of tillage operations, the preparation of a suitable seed bed and to the reclamation processes.

Physiological and bio-chemical importance of sodium in animal nutrition cannot be over-emphasised. Its functions in body fluids *e.g.* blood, serum etc. regulating pH and activity of cell are very well known to bio-chemists and physicians.

It is therefore clear how important it is to adopt a suitable and accurate method for estimation of this base. Until recently sodium was determined in many Indian laboratories by difference. Sodium and potassium were usually converted, by Puri (1933) and others, into chlorides or sulphates and from this mixture the amount of potassium determined separately was subtracted and the balance worked out as sodium. This indirect estimation by difference is open to great criticism. It is not only laborious, but is subject to considerable errors.

The gravimetric method as followed by Barber and Kolthoff (1928), Kahane (1930) and Piper (1932) is also unsuitable and inaccurate in presence of very small amounts of sodium. Whilst

the degree of accuracy attained by these workers leaves nothing to be desired, the manipulative details are somewhat troublesome. Some ten to fifteen washings are necessary in order to transfer the precipitate to the filter and to remove the last traces of the reagent. This procedure involves the risk of errors due to leaching even when the wash medium is saturated with the triple salt, to the introduction of extraneous matter and to possible variation in the degree of hydration of the precipitate.

The volumetric method due to Blenkinsop (1930) carried out by Mackness (1930), Mulwani and Pollard (1937), in spite of its accuracy is very tedious and involves use of reagents which could only be handled by expert analysts.

The colorimetric method, as worked out by Barrenscheen and Messiner (1927), McCance and Snipp (1931), Mulwani and Pollard (1937), is very easy, and most accurate and applies to soils, plants and biological materials. Mulwani and Pollard (1937) working on soils have compared with the volumetric method and have presented ample evidence of its accuracy and the ease with which it works. Large amounts of soluble phosphates and organic matter interfere but in the case of soils a further point of interest is that usually such soluble substances are not high enough to affect the determination. The method as devised by McCance (1931) on biological material has been further curtailed and simplified by the writer. The extra reagent (alcoholic zinc-acetate-hydroxide) employed by McCance to separate phosphate is eliminated in the simplified method. The sodium is precipitated as the triple acetate with uranium and zinc. The uranium in the precipitate is estimated colorimetrically with potassium ferrocyanide. As this short method is more or less new to many soil workers in India it has become necessary to present a description of the method along with details for preparation of the reagents employed.

PREPARATION OF RE-AGENTS AND STANDARDS

(1) *Alcoholic uranyl zinc acetate reagent* (modified from Kolthoff, 1927).

(a) Dissolve 20 g. of uranyl acetate in 100 cc. of boiling water containing 5 cc. of glacial acetic acid. (b) Dissolve 60 g.

of zinc acetate in 100 cc. of boiling water containing 2 cc. of glacial acetic acid.

Mix both solutions, while boiling, raise the temperature again just to boiling, allow to stand over night and filter. Mix the filtrate with an equal volume of absolute alcohol. Allow to stand 24 hours at 0° and filter at 0° . The reagent is stable at room temperature.

(2) *95 per cent alcohol saturated with the triple acetate.*—Prepare a sample of sodium-uranyl-zinc-acetate by adding the uranyl-zinc-acetate reagent to some NaCl dissolved in 50 per cent alcohol. Filter and wash the precipitate thoroughly with 95 per cent alcohol. Suspend the precipitate in 95 per cent alcohol and allow to settle in the ice-chest. Use the supernatant fluid for washing the precipitate. Filter before use if not absolutely clear.

(3) *20 per cent. Potassium ferrocyanide solution.*

(4) *Standard sodium chloride.*—Dissolve 1 g. of pure dry NaCl A.R. in water and make upto 100 cc. This forms the stock solution. For use dilute 2 cc. to 100 cc.; 1 cc. of this dilute standard contains 0.2 mg. NaCl (0.0786 mg. Na).

(5) *Standard triple acetate.*—(a) Preparation of the stock solution. Take 10 cc. of 1 per cent solution of NaCl, add 80 cc. of water +100 cc. of alcohol. Add 100-120 cc. of zinc uranyl acetate reagent. Stand for at least an hour. Collect this precipitate quantitatively and wash it carefully with ice-cold 95 per cent. alcohol. Dissolve the precipitate in water and make up to 1000 cc. This forms the stock solution. Dilute some of this accurately 1 to 5. Take 10 cc. of this weak solution, dilute with water in a 25 cc. flask. Add 1 drop of glacial acetic acid and 0.5 cc. 20 per cent potassium ferrocyanide. Make upto 25 cc. The resulting colour is close to that obtained from 0.2 mg. NaCl (0.0786 mg. Na) in 2 cc. of water submitted to all stages of the method and made upto 25 cc. (b) Standardisation of the solution.—This should be done at least in quadruplicate. Take four samples of exactly 0.2 mg. NaCl (0.0786 mg. Na) in 2 cc. of water and subject them to every stage of the estimation. Transfer the precipitate to 25 cc. flasks. In two other flasks take 10 cc. of the dilute standard and add water to about 18-20 cc. Develop the uranium colour as described above in

all six 25 c.c. flasks. Match both standards against each of the quadruplicate flasks. They should agree with each other.

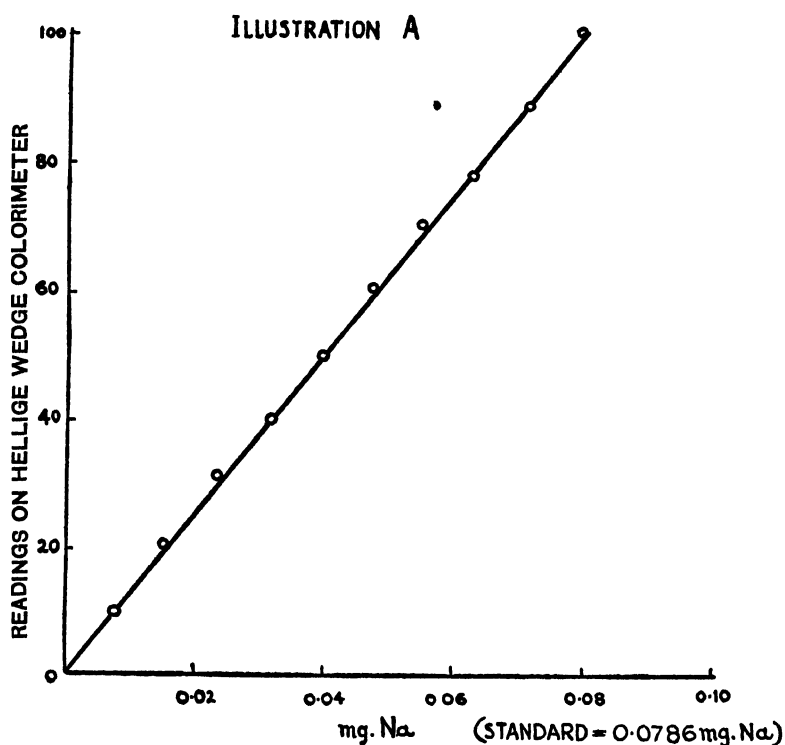
Detailed description of the simplified procedure is as follows:—

A solution or extract containing 0.01 to 0.60 mg. of sodium is taken in a pyrex centrifuge tube and volume made to 2.0 cc. with water. 4.0 cc. of the uranyl zinc acetate reagent (sufficient to precipitate 0.8 mg. of Na) are added and stirred with a pointed glass rod. Stirring is continued until the precipitate begins to appear. The tube is covered and allowed to stand for an hour at 0°. After centrifuging for four minutes at 3000 r.p.m. the clear liquid is poured off and the tube drained by inverting on filter paper. The mouth of the tube is wiped off with a piece of filter paper and washing is done once only with 5 cc. of the ice-cold alcohol saturated with the triple salt. Care is taken to see that the whole of the inside of the tube is rinsed. After stirring up the precipitate the tube is centrifuged for four minutes and the liquid drained off. The precipitate is dissolved in water and transferred quantitatively to a 25 cc. volumetric flask. If the precipitate is very bulky, indicating that the unknown contains more than 0.078 mg. Na, it is transferred to a 50, 100 or even 200 cc. flask according to discretion. After a little experience it is easy to judge the size of the flask required from the bulk of the precipitate.

For the standard either 0.5 cc. of the dilute Na Cl solution (containing 0.1 mg. Na Cl) is taken and treated exactly in the same way as the unknown and transferred to a 25 cc. flask or 5 cc. of the dilute standard triple acetate solution taken in a 25 cc. flask. To both standard and unknown are added a drop of glacial acetic acid and 0.5 cc. of 20% potassium ferrocyanide, and volume made upto the mark. The colour developed after one minute's shaking is matched in colorimeter.

In the case of Hellige Wedge Colorimeter graphs may be prepared with different standards. This will afford an easy calculation of results. (See Illustration A).

Table I records the results obtained with gravimetric, volumetric and colorimetric methods. Those interested to have fuller data on these methods are advised to refer to the publications cited under references.



	Mg. Na. taken			Theoretical reading			Actual reading
1.	0.00786	...	...	10	...	...	10
2.	0.01572	...	...	20	...	...	21
3.	0.02358	...	...	30	...	...	31
4.	0.03144	...	...	40	...	...	40
5.	0.03930	...	...	50	...	...	50
6.	0.04716	...	...	60	...	...	60
7.	0.05502	...	...	70	...	...	72
8.	0.06288	...	...	80	...	...	78
9.	0.07074	...	...	90	...	...	89
10.	0.0786	...	...	100	...	...	100

TABLE I
Recovery of sodium by different methods.

Mg. of sodium taken	Mg. of sodium recovered		
	1. Gravimetric method	2. Volumetric method	3. Colorimetric method
0.0393	0.0626	0.0390	0.0394
0.0786	0.0923	0.0795	0.0785
0.157	0.152	0.160	0.158
0.236	0.229	0.238	0.235
0.314	0.338	0.289	0.314
0.393	0.399		0.393
0.472	0.481		0.473
0.550	0.562		0.551
0.630	0.653		0.630

Note :—1. Pure sodium chloride (A. R.) was used.

2. The values given in the table are average of four replications.

3. Previous experience has shown that the volumetric method becomes somewhat less reliable in the range 0.3 to 1.0 mg. of sodium.

Lowest limits of the determination were obtained only with the colorimetric method. For very small amounts of sodium the precipitate of triple salt was dissolved in a minimum volume of water and the ferrocyanide colour developed in 5 cc. instead of 25 cc. In this way the following data were obtained :—

TABLE II
Lowest limits of sodium determination.

Mg. NaCl taken	Mg. NaCl recovered (average of 4 replications)
0.002	0.003
0.004	0.004
0.006	0.006
0.010	0.010
0.020	0.020

It is clear that the colorimetric method works well in the presence of as low as 0.004 mg. of sodium chloride (0.00157 mg. Na).

CONCLUDING REMARKS

1. The Micro-colorimetric method is described by which 0.004 to 0.6 Mg. sodium can directly be determined.
2. Ca, Mg, Fe, Al and Mn do not interfere. Acidity upto 2.2 N. Hcl does not affect (*vide* Mulwani and Pollard, 1937).
3. Large amounts of potassium (exceeding four times the weight of sodium present) may be removed by pretreatment with perchloric acid.
4. Colorimetric method considerably saves time and operates over much larger range of concentration of sodium with greater accuracy than any other method. With a good centrifuge machine accomodating at least eight centrifuge tubes forty determinations could be done in a full day.

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List of theses in Botany, Zoology, Agriculture and Medicine which have been accepted in lieu of the Examinations for the degrees of M.Sc., Ph.D., D.Sc. and M.D. during the year 1939-40

Subject	Title of the thesis	Name of the candidate	Teacher	Place of research	Remarks
FOR THE DEGREE OF M.Sc.					
Botany	Effect of H-ion concentration of different salt solutions on the growth of rice seedlings.	Mr. D. V. Sohance	Prof. R. E. Cooper	Royal Institute of Science, Bombay.	
Do.	Some morphological observations on <i>Loranthus Longiflorus</i> Des.	Mr. T. D. Desai	Prof. S. V. Shevade	Baroda College, Baroda.	
Do.	Study of the morphology of the Rice plant (<i>Oryza sativa</i> L. Colimbe variety No. 42).	Mr. H. H. Dubash	Prof. R. H. Dastur	Royal Institute of Science, Bombay.	
Do.	A contribution to the Ecological Foliar Anatomy of Indian Plants.	Mr. J. L. Desai	Prof. J. F. R. d'Almeida	St. Xavier's College, Bombay.	
Zoology	(i) The Biology of the food fishes of Mahim creek; (ii), Anatomy of <i>Scotophagus argus</i> ; (iii) The Digestive enzymes of the pyloric caeca of <i>Scotophagus argus</i> ; (iv) The Musculature and Movement of the Dragon fly larva.	Mr. N. S. Desai	Prof. C. J. George	Wilson College, Bombay.	

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Subject	Title of the thesis	Name of the Candidate	Teacher	Place of research	Remarks
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Botany	A Study of the Genus <i>Ophioglossum</i> in India.	Mr. T. S. Mahabale			
Do.	A Study of the Pistillate plants of <i>Ephedra foliata</i> Boiss, found at Drigh Road, near Karachi, Sind.	Mr. B. N. Mulay		D. J. Sind College.	
Agriculture	(i) Sewage in India with special reference to investigations into problems affecting disposal of Poona Sewage by Irrigation ; (ii) Disposal of Poona Sewage Effluent.	Mr. D. G. Kulkarni			
Zoology	A Contribution to the study of Indian Copeognatha.	Mr. M. G. Ramdas Menon	Prof. C. J. George	Wilson College, Bombay.	
FOR THE DEGREE OF D.Sc.					
Botany	Contributions to the Systematics of the Malayan Palms.	Mr. C. X. Dos R. Furtado			
FOR THE DEGREE OF M.D.					
Pathology	Diagnostic Methods and Prophylaxis of Typhoid Fever.	Mr. P. M. Wagle		Seth G. S. Medical College.	

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